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# LOWER CLARK FORK
# WATER QUALITY MONITORING
# 1984 - 1985

## VOLUME II
## SPECIAL STUDIES

Prepared by:

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December 1985

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## I. Introduction

This report comprises the second of two volumes of water quality information collected by the Department of Health and Environmental Sciences' (DHES) Water Quality Bureau (WQB) and others on the lower Clark Fork River and its major tributaries in 1984 and 1985. As discussed in the introduction to Volume I, the purpose of the data collection was to 1) establish chemical, physical and biological water quality baseline information for the lower Clark Fork River, 2) measure changes in water quality resulting from modifications in the Champion International Frenchtown Mill wastewater discharge permit and, 3) to determine contributions, effects and fates of water quality contaminants from various wastewater sources and tributaries along the river.

The WQB's decision to study the river was in part due to questions raised by the public concerning the 1983 decision to give Champion a two-year permit to allow year around direct discharge of treated wastewater to the Clark Fork. Following the Preliminary Environmental Review (PER) the WQB announced its decision to issue a two-year discharge permit, study the river during that period and prepare an Environmental Impact Statement (EIS) prior to issuance of a new permit in April 1986. A river monitoring plan was included in the PER.

Volume I presents the methods and tabulated results of the WQB's Clark Fork River monitoring for the period March 1984 through August 1985. Also included are other supporting data such as streamflow records and self-monitoring information for the major permitted wastewater discharges to the river. Volume II is a collection of reports giving the findings of special studies designed to investigate areas of special concern in the lower Clark Fork system, primarily the instream consequences of the wastewater discharge from the Champion mill.

## II. General Descriptions of the Special Studies

The nine special studies described in this report include:

1. Aesthetics Monitoring was performed by the WQB, Montana State University, Oregon State University and others. The intent of this group of investigations was to address the question of impaired river aesthetics due to Champion's discharge of wastewater. Activities included: general field reconnaissance, river and wastewater foaming tendency and stability tests, analysis for the presence of foaming agents, organic analysis of river and wastewater foam, microscopic examination of river, wastewater and foam suspended solids and the evaluation of fish flesh tainting (odor and flavor) due to the Champion discharge.

2. Algal bioassays of Clark Fork River water were done by the Environmental Protection Agency (EPA) Region X's Corvallis Environmental Research Laboratory. These tests determined, on a seasonable basis, which nutrients limited algal growth in the river and if metals toxicity was a factor controlling algal productivity. These studies will provide the ability to predict some of the

instream consequences of increased nutrient loading rates by the Champion mill.

3. Chronic bioassays of the Clark Fork River and Champion wastewater were conducted by EPA Region VIII. These tests on juvenile rainbow trout and a water flea, *Ceriodaphnia*, helped to predict the effects of the wastewater and other river contaminants on the growth and reproduction of the river's aquatic life.

4. A status report on a major fisheries study of the lower Clark Fork discusses the work being done by the Department of Fish, Wildlife and Parks (DFWP). This study will inventory the kinds and numbers of fish present in the lower Clark Fork system and assess the effects of pollutants on fish numbers, reproduction and general health.

5. A riffle community metabolism study by the University of Montana measured the effects of Champion's wastewater discharge on metabolic rates of the Clark Fork's bottom-dwelling plants and animals.

6. An evaluation of the lower Clark Fork's macroinvertebrate community was made by C.E. Hornig. This evaluation, which provided baseline information and examined the effects of wastewater discharges, was based on the unevaluated data (species lists, counts, key statistics) tabulated in Volume I.

7. A study of copper concentrations in Clark Fork River crayfish was done by the DFWP. This investigation attempted to evaluate the concern that oxygen-demanding organic solids in the Champion discharge could settle in slow-water areas, causing metals tied up in stream sediments to become soluble and thereby becoming mobile and available to plant and animal life.

8. The University of Montana conducted a Clark Fork reservoir sediment study, which examined the chemical makeup of bottom sediments, particularly metals, in the river's impoundments.

9. A summary is provided of the State of Idaho's continuing Lake Pend Oreille study. This project is examining the lake's water quality and trophic status as influenced by its major tributary, the Clark Fork River.

## III. Methods and Results

A separate report describing the methods and findings of each special investigation follows in the pages ahead. Further discussion of these study results and the possible ramifications of the increased wastewater discharge from the Champion mill may be found in the Champion draft EIS.

# A. AESTHETICS MONITORING

# Aesthetics Monitoring of the Clark Fork River in the Vicinity of the Champion Frenchtown Mill Wastewater Discharge

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## INTRODUCTION

In the fall of 1983, the Water Quality Bureau (WQB), Montana Department of Health and Environmental Sciences (DHES), prepared a Preliminary Environmental Review (PER) on a proposed waste discharge permit for Champion International's Frenchtown Mill. During the public involvement process, many people expressed concern over perceived aesthetics problems in the Clark Fork, downstream of Champion's wastewater discharge. Complaints included an apparent increase in river foam, reports of a dirty film on the water surface, foul-smelling water and catches of off-flavor fish.

In an attempt to investigate and address the question of impaired aesthetics due to wastewater discharges to the Clark fork, the WQB conducted several aesthetics monitoring activities during an 18 month study of the river. In addition, several fish flavor and odor evaluations were performed through the cooperative efforts of Champion International, the Montana Department of Fish, Wildlife and Parks, Montana State University and Oregon State University.

The U.S. Environmental Protection Agency (EPA) funded the WQB's portion of this investigation through its sponsorship of the WQB's Lower Clark Fork River Water Quality Study. Champion funded the fish tainting studies, which are required under its Montana Pollutant Discharge Elimination System (MPDES) wastewater discharge permit.

The rationale, methods and results of each aesthetics monitoring activity are presented in the following pages.

## AESTHETICS RECONNAISSANCE

Rationale: Verification of citizen complaints by the regulatory agency is the first step toward correction of the problem(s).

Methods: During the course of the lower Clark Fork water quality study, WQB field personnel looked for and recorded any incidental evidence of water quality degradation and reduced river aesthetics. A written and photographic record of such observations was made, particularly the presence and character of foam, sludge deposits, slime growth, stained rocks, colored or cloudy water, foul-smelling water and surface film.

Results: During the 1984-1985 water quality study, numerous documentations were made of reduced aesthetics along the lower Clark Fork and its major tributaries. In many of the cases, causes of the problems were obvious, in others, they were less apparent. A summarization of the most notable problems reducing aesthetics and/or recreational potential in the river system is given by stream reach in Table 1. Observations of less significant aesthetics problems have not been described and it is possible some problems have been overlooked. The reader is referred to Appendix C in Volume I of the Data Report for a condensed version of field notes taken during the study, which describe the observed river conditions.

Table 1. Aesthetics Reconnaissance Summary

| Stream Reach | Problem |
|---|---|
| Clark Fork below Milltown Dam to confluence of Bitterroot River | The aesthetics of this reach were reduced during the annual operational drawdowns of Milltown Dam in July 1984 and June 1985, due to increased turbidity. |
| Clark Fork in the immediate vicinity of and extending for more than 400 yards below the Missoula WWTP discharge. | The WWTP was significantly more turbid than the river during 15 of 25 observations. Frequently it was highly turbid, colored, foamy and foul-smelling. The river in the plume of the discharge and for a considerable distance downriver had an increased turbidity and a noticeable sewage odor. Foam contributed by the discharge dissipated rapidly. |
| Bitterroot River near mouth. | Sizeable accumulations of a dirty yellow foam were present along shoreline areas in early spring to early summer, (except during peak runoff) and again in the fall. |
| Clark Fork from 0.5 miles below the Champion mill discharge to to the confluence of Petty Creek. | Large, lofty patches of a dirty yellow to brown foam were frequently observed on the river surface. Accumulations were noted in various areas near shore, especially in the Ninemile area. The problem occurred year around but was noticeably worse in spring and fall. Concentrations of apparently organic particulate matter frequently appeared to be higher in this reach of river than above the Champion mill. Just below the Champion mill, several localized areas of high river color (tea-colored water) were present near the shorelines where Champion wastewater pond seepage surfaced. These areas were usually accompanied by a stained river bottom. |
| Clark Fork from St. Regis to the confluence of the Flathead River. | Large accumulations of dirty foam were observed near shoreline areas and in eddys and backwaters in early spring and again in the fall. |

| Stream Reach | Problem |
|---|---|
| Flathead River near mouth. | River stage fluctuated significantly over a 24-hour cycle, apparently due to the peaking power operation of Kerr Dam upstream. Wet shoreline areas at low stage reduced aesthetic appeal. |
| Clark Fork from Flathead River confluence to Plains. | Fluctuating river stage due to influence of Flathead River resulted in exposed shoreline areas and an unstable aquatic environment. Exposed river algae contributed to odor problems. |
| Clark Fork from Thompson Falls Dam to Noxon Rapids Reservoir. | River stage fluctuated daily due to the operation of Thompson Falls Dam and created the same problems which occurred at the two previous locations. Spring drawdowns of Noxon Rapids Reservoir downstream resulted in major changes (up to 10 feet) in river stage in this reach in March 1984 and May 1985. The large scale 1985 drawdown exposed large areas of riverbed, created odor problems as algae decomposed and practically eliminated recreation due to poor river access and the treacherously slippery river banks. Spilling at Thompson Falls Dam during spring runoff created sizeable patches of clean, white foam but it was not a particularly significant aesthetic problem. |
| Noxon Rapids Reservoir. | The previously mentioned drawdowns in 1984 and 1985 significantly reduced the aesthetics of the reservoir and the recreational potential. The 1984 drawdown was not particularly large compared to 1985 when the reservoir was lowered from 35 to 50 feet. However, in both cases reservoir turbidity was increased as tributaries feeding into the impoundment began headcutting their beds and banks and exposed mud flats dewatered. The presence of stranded, dying and dead fish in 1985 was particularly unaesthetic. |

| Stream Reach | Problem |
|---|---|
| Clark Fork below Noxon Rapids Dam and below Cabinet Gorge Dam. | Apparent peaking power operation of both dams resulted in frequent and significant fluctuations in river stage. Problems were similar to those in the Flathead, at Plains and below Thompson Falls Dam. Exposed mud bars below Cabinet Gorge Dam created access problems. Spilling of water over the dams in spring created white foam but it was not a significant problem. |

## RIVER AND WASTEWATER FOAMING TENDENCY AND STABILITY, QUANTITATIVE SURFACTANT TESTING AND FOAM ANALYSIS

### Rationale

During the early part of the water quality study, field personnel noticed significant accumulations of river foam at several locations along the Clark Fork--both above and below Champion--and in some of the tributaries, most notably the Bitterroot River.

River foam did appear to be more common below the Champion discharge. Since quantification of the actual amount of foam present along the river would have been difficult, study personnel investigated other methods of determining the relationship between lower river foam and the Champion discharge. Several methods were used.

### Methods

Foam can be classified according to its ability to form and persist.

A procedure is available for measuring foaming tendency and foam stability in terms of equivalent concentrations of detergent. Although it was developed for pulp and paper mill effluents, it can be used on natural waters and other types of effluents, including the effluent from the Missoula wastewater treatment plant (WWTP). It was expected that this test would assess the relative importance of wastewater effluents and natural agents as foam producers in the Clark Fork River system.

The methylene blue active substances (MBAS) test is a quantitative test which indicates the relative concentration of surface-active agents or surfactants. Surfactants are the responsible agents in the formation of foam on rivers and streams. The test was designed to detect the presence of detergents in municipal wastewater discharges. It is known that some wastewater constituents cause interferences in the test results. Nonetheless, the test was conducted on the Champion wastewater discharge and the Clark Fork above and below Champion in order to investigate its applicability.

A final method of investigating the perceived river foam problem involved physically collecting a large volume of foam at two control and three test stations by means of a hand operated vacuum pump. The foam liquified as it was vacuumed up, solid materials were allowed to settle and from one to three liters of the liquid were analyzed for the same organic constituents and in the same manner (GC/MS) as the Champion wastewater samples described in Volume I of this report. The presence, in relatively high concentrations, of organic constituents unique to the Champion wastewater in downstream river foam would link the downstream foam to the waste water discharge.

The solid materials from the foam samples were examined microscopically to determine their composition and a relative abundance estimate was made of each component identified. It was felt that this solids examination might provide further clues to the origin of the foam.

Sample collection and analysis methods of the various foam tests are shown in Table 2.

## Results

Each of the three tests described above was performed once during the study on a series of river and wastewater samples. The results are given in the following pages.

### Foaming Tendency and Stability

Unpreserved grab samples for the foaming tendency and stability tests were collected in March 1984 from the following river and effluent monitoring stations: 06-Clark Fork above Missoula WWTP; 07 - Missoula WWTP discharge, 09 - Clark Fork two miles below Missoula WWTP; 10 - Bitterroot River near mouth; 11 - Clark Fork at Harper Bridge (above Champion); 12 - Champion discharge, 15 - Clark Fork at Huson (below Champion), 20 - Clark Fork at Superior, 23 - Flathead River near mouth and 25 - Clark Fork above Thompson Falls Reservoir. Samples were transported on ice to the DHES Chemistry Laboratory. Foaming tendency and stability testing produced positive results only on the sample of Champion wastewater. All other samples produced results less than the detection limits of the tests. Results are presented in Table 3.

Table 3. Results of the Foaming Tendency and Stability Tests

| Station | Foaming Tendency (as mg/l LAS) | Foaming Stability (as mg/l LAS) |
|---|---|---|
| 06 | <2 | <5 |
| 07 | <2 | <5 |
| 09 | <2 | <5 |
| 10 | <2 | <5 |
| 11 | <2 | <5 |
| 12 | 10 | 17 |
| 15 | <2 | <5 |
| 20 | <2 | <5 |
| 23 | <2 | <5 |
| 25 | <2 | <5 |

### MBAS Test

River water from stations 11 and 15 and the Champion wastewater (12) were sampled for MBAS testing in February 1985 and transported refrigerated to the DHES Chemistry Laboratory. Like the foaming tests, only the Champion wastewater produced a positive test. However, interfering agents apparently were present in the wastewater. The MBAS test results for that sample and the river sample collected downstream from the wastewater discharge may not be accurate. Table 4 gives the test results and lab remarks regarding the interferences.

Table 2. Sample Collection and Analysis Methods for Foam Testing

| Variable | Collection Method | Analytical Method | Laboratory |
|---|---|---|---|
| Foaming Tendency and Stability (as mg/l LAS) * | Grab Sample | TAPPI 1) | MDHES Chem Lab |
| Methylene Blue Active Substances (MBAS) Test (mg/l) | Grab Sample | EPA 425.1 2) | MDHES Chem Lab |
| Foam GC/MS Priority Pollutant and Scan Analysis (ug/l) | Suction Pump | EPA 608 3)<br>EPA 624 3)<br>EPA 625 3)<br>EPA 1624 3)<br>EPA 1625 3) | EPA Region VIII Chem Lab |
| Foam Solids Analysis | Suction Pump | Microscopy | MDHES WQB |

References

1)"Measurement, Control, and Changes in Foaming Characteristics of Pulping Wastes during Biological Treatment," W.L. Carpenter and I. Gellman in TAPPI Journal, Vol.50, No. 5, May 1967.

2)"Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, U.S. Environmental Protection Agency, 1983 (Revised).

3)Federal Register, Vol. 49, No. 209, Appendix A, October 26, 1984.

* A modification of the referenced analysis method was utilized. LAS (linear alkyl sulfonate) was used as a reference material instead of ABS (alkyl benzene sulfonate). Hence, results are expressed in terms of equivalent concentrations of LAS in mg/l.

Table 4. Results of the Methylene Blue Active Substances (MBAS) Test

| Station | MBAS (mg/l) | Lab Remarks |
|---|---|---|
| 11 | < .005 | Sample formed no scum during the extraction phase of the test. |
| 12 | .710 | Sample formed an unbreakable emulsion during extraction and had to be diluted. A 1:20 dilution also formed an emulsion but not as badly. The test result is most probably low. |
| 15 | < .005 | Sample formed a very slight scum during the extraction which may have been due to wastewater influence. |

## Organic and Microscopic Foam Analysis

Samples of surface foam were collected at stations 06, 10, 16 (Clark Fork at Ninemile), 21 (Clark Fork below St. Regis) and 12 (Champion wastewater storage pond number 10) during the week of September 22, 1985 and transported refrigerated to the laboratory.

The results of the GC/MS analysis of the foam samples performed by the U.S. EPA Region VIII Laboratory in Denver were not available at the time of report preparation. A Table 5 containing these data will be distributed as a supplement in the near future. Descriptions of the solid materials identified in the foam samples and the condition and relative abundance of each component follow in Table 6.

Table 6. Microscopic examination of solid materials in the river and wastewater foam samples

### 06 - Clark Fork at Reserve Street

diatom algae (mostly decadent or dead periphytic forms) - abundant
desmid algae (*Cosmarium* and *Closterium*, healthy or decadent) - common
misc. algae (mostly decadent or dead) -rare
insects (primarily dead adult midges) - rare
insect parts (exuviae, head cases, legs, antennae, exoskeleton fragments) - very common
fungi (primarily Fungi Imperfecti associated with plant matter) - very common
bacteria (masses of cells, not clearly associated with organic matter) - very common
organic matter, FPOM (allochthonous plant fragments, unidentified amorphous masses) - common; pollen - rare.
inorganic matter (very fine sand and silt particles) - common

## 10 - Bitterroot River Near Mouth

diatom algae (mostly decadent or dead periphytic forms) - abundant.
desmid algae (*Closterium* and *Staurastrum*, appeared healthy ) - common.
other algae (*Scenedesmus*, *Oscillartoria*, *Pediastrum* and *Dactylococcopsis*, healthy or decadent) - common
insects (adult midges) - common
insect parts (exuviae, legs, exoskeleton fragments) - very common
fungi (primarily Fungi Imperfecti associated with plant matter) - very common
bacteria (single cells and aggregates) - very abundant
organic matter, FPOM (allochthonous plant fragments) - very common; pollen rare
inorganic matter (very fine sand and silt particles) - uncommon

## 12 - Champion International Pond 10

algae:
- *Oscillatoria* (appeared healthy) - abundant
- *Chlamydomonas* (decadent or dead) - abundant
- *Euglena* (motile, healthy) - rare
- diatoms (decadent or dead) - rare

insects or insect parts - none present
protozoans:
- ciliates (motile, healthy) - rare

testaceous amoebas? (tests or shell only) - very common
bacteria:
- *Chromatium*? (purple sulphur bacteria ) - abundant
- *Macromonas*? and *Thiothrix*? (colorless sulfur bacteria) - common
- other (unidentified rods, coccoids) - very common

fungi (Fungi Imperfecti?) - rare
organic matter, FPOM:
- unidentified amorphous masses (10-100 um diameter; cellulose?) - abundant
- allochthonous plant fragments - uncommon

inorganic matter - not apparent

## 16 - Clark Fork at Ninemile

algae:
- diatoms (mostly decadent or dead, some healthy) - very common
- *Oscillatoria* (appeared healthy) - common
- *Staurastrum*, *Scenedesmus*, *Cosmarium*, and *Chlamydomonas* (appeared healthy) - rare

insect parts (exuviae, antennae) - common
fungi (Fungi Imperfecti) - very common
bacteria (rods, coccoids, motile "spirillum") - very common
- sulfur bacteria not apparent

protozoans:
- ciliates - common
- amoeba (tests only) - rare

organic matter, FPOM, (unidentified amorphous masses, 100-200 um diameter; cellulose?) - very common
inorganic matter (very fine sand and silt particles) - common

### 21 - Clark Fork below St. Regis

diatom algae (mostly dead) - common
other algae (*Scenedesmus*, *Pediastrum*, and *Cosmarium*, appeared healthy) - rare
insects (deal adult midges) - uncommon
insect parts (exuviae, mandibles, and antennae) common
fungi:
- Fungi Imperfecti (characteristic tetrahedral hyphae) - very common
- other fungal hyphae (long, relatively large diameter) - common

bacteria (mostly rods, few motile spirillum) - very common
organic matter, FPOM:
- unidentified amorphous masses (some 100 um; cellulose?) - very common
- allochthonous plant fragments - uncommon

inorganic matter (very fine sand and slit) - uncommon

## CHAMPION WASTEWATER MICROSCOPIC ANALYSIS

### Rationale

The WQB had received a number of complaints from citizens who noticed shoreline deposits of dried organic material resembling paper fibers that were believed to have originated form the Champion Kraft Mill wastewater discharge. Several samples of this material proved to be dehydrated river algae left exposed along the river banks when high water receded. In order to determine conclusively the nature of solid materials in the Champion wastewater and to address the public concerns, samples were collected on a routine basis for microscopic examinations.

### Methods

Beginning in October, 1984, unpreserved grab samples of Champion wastewater were collected at least monthly for microscopic examination and identification of constituent living and non-living materials

### Results

Results of the microscopic analyses of the Champion wastewater are given in Table 7.

Table 7. Microscopic Examination of Solid Materials in Champion Wastewater Samples.

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| 10/15/84 | 003 | 150 ml filtered. Euglena sp. (Large-35 u long, green, with red eyespots), abundant.<br>Chlorella (?) (small-5 to 10 u diameter, green spheres, without eyespots), abundant.<br>Diatoms (Nitzschia, Navicula, Synedia, Diatoma, Cymbella some living, common.<br>Bacteria? Yeast? (very small - 1 u diameter colorless cells, solitary or in small clusters), extremely abundant.<br>Misc. spores, eggs, cysts, etc., common. |
| | Clark Fork River at Harper Bridge | Material on filter paper: Diatoms very abundant. Detritus common. |
| | Clark Fork River at Huson | Material on filter paper: Diatoms very abundant. Detritus common. |
| 11/15/84 | 003 | Phacus sp. common, Euglena sp. rare (1 observed), Chlamydemenas sp. (?) fast-swimming green flagellate (very small compared to Phacus), Chlorella sp. rare, Ankistrodesmus sp. rare (1 observed), stalked ciliated protozoan ("). Very small (smaller than Chlamydomonas) dark-colored (not green) and motile protozoans very common. Bacteria (?) detritus ? "color bodies"? Extremely small ( 1 u diameter) and extremely abundant. Sample given to Anne Poor, DHES Microbiology Laboratory, for agar smear. No large swimming organisms and no paper (wood) fibers visible.<br>From Anne Poor, DHES Microbiology Laboratory: Champion discharge received 11/15/14, Bacteria: Bacillus sp. predominant, 2 gram negative rods, 1 gram positive cocci. Fungi: Penicillium sp., Streptomyces sp. Champion discharge received 11/21/84 similar if not identical mix of bacteria and fungi. Aerobic, common stuff nothing unusual or pathogenic. |

Table 7. Continued

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| 12/11/84 | 003 | Besides the usual fungi and bacteria, sample contained *Phacus* and a variety of green and colorless flagellates. One globe-shaped green flagellate had flagella of unequal length, one much longer than the other. |
| 1/14/85 | Pond 12 Overflow | Sample contained mostly bacteria, clumps of bacteria and clumps of non-descript particulate organic matter. Contained a few very small colorless flagellates. No algae observed, however sample was stored (in refrigerator) for one month prior to analysis.<br>Nothing resembling wood or paper fibers was observed. |
| 2/21/85 | 003 | Effluent contained mostly very small particles, presumably bacteria, of several shapes, including round, rod and a few *Spirillum*-shaped cells. A very few large, colorless zooflagellates were present. No algae. (Ponds ice covered.) A few structures that may have been sulfur bacteria.<br>Amorphous organic detritus present; nothing resembling wood or paper fibers. |
| 3/18/85 | 003 | Sample smelled distinctly of hydrogen sulfide. Dominated by bacteria, fungi and very small, finely divided particulate organic matter with scattering of colorless flagellates and ciliates.<br>No algae or wood cells or higher animals (crustaceans, rotifers, etc.) present.<br>Several of the same structures present as observed in the February collection. |
| 4/10/85 | 003 | Sample odor and color were typical of Champion effluent. Dominated by bacteria, including unicellular rod, ovoid, "vibrio" and "spirillum" forms, filamentous rods and aggregates of rods and ovoid forms. Some possessed sheaths, capsules or flagella. The green sulfur bacteria *Chlorochromatium aggregatum* was less common but quite distinctive, resembling a motile "bunch of |

Table 7. Continued

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| | | grapes". (May have been the colorless sulfur bacterium Macromonas.)<br>No fungal hyphae were found. Three genera of algae were identified: the green algae Chlorella, which was fairly common, and the blue-greens Chroococcus and Oscillatoria, both of which were rare.<br>A single ciliate was observed. No other protozoans or higher animals were found.<br>The sample contained a fair amount of fine particulate organic matter, but nothing identifiable as wood cells or paper fibers. |
| 4/23/85 | 003 | Sample odor and color typical of Champion effluent. Again dominated by a diverse variety of bacteria. Flagellated, colorless unicellular bacterium with distinctive globules within membrane (resembled "bunch of grapes") very common. Appears to be colorless sulfur bacterium Macromonas. Also filamentous form with globules (sulfur bacterium Thiothrix?). Both stained gram negative. Another filamentous bacterium resembled blue green algae Oscillatoria, only very narrow and colorless. No fungi were identified.<br>Algae included Chlorella (common), Chlamydomonas (rare) and one individual of Euglena gracilis.<br>Ciliated and flagellated protozoans were rare. Stalked rotifers were present amongst bacteria filaments.<br>Fine particulate organic matter was common, but nothing identifiable as wood cells or paper fibers were present. |
| 5/8/85 | 003 | Sample color and sulfurous odor was typical of previous Champion effluent samples. |

Table 7. Continued

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| | | Biota again was dominated by many forms of bacteria. The motile colorless sulfur bacterium *Macromonas*, and what appeared to be the motile purple sulfur bacterium *Chromatium* were very common. Other non-motile, colorless coccoids with distinctive "sulfur" globules were very numerous. Filamentous forms were relatively rare. No fungal filaments were identified.<br>Algae included *Chlamydomonas* and *Phacus* (both common) and *Euglena* and *Chlorella* (both rare).<br>Colorless ciliated protozoans were common. No rotifers or other animals were seen.<br>Fine particulate organic matter was fairly common, but nothing identifiable as wood or paper fibers were seen. |
| 5/22/85 | 003 | Sample color and sulfurous odor again typical of previous Champion effluent samples.<br>Biota was dominated by many forms of bacteria, although algae were more common than before. Purple sulfur bacteria were abundant with what appeared to be *Thiothece* the most common and the motile forms *Chromatium* and *Thiospirillum* less numerous. Thin filamentous green or colorless bacteria were also common. The motile colorless bacterium *Macromonas* was rare in this sample.<br>Algae included *Phacus* (2 or 3 spp.) which was very common, *Euglena*, *Chlamydomonas* and *Chlorella* which were common, and *Oocystis* which was rare.<br>Colorless flagellated protozoans (mistaken as ciliates in the last few samples) were very common.<br>Fine organic particles were relatively rare, and no wood or paper fibers were seen. |

Table 7. Continued

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| 6/5/85 | 001 and 003 | Color and odor of effluent samples typical of previous samples. Biota again dominated by many forms of bacteria. |
| | | Discharge 001 contained primarily non-motile forms, probably *Chromatium* and/or *Thiothece* purple sulfur bacteria, plus unidentified rods and spheres. |
| | | Discharge 003 contained non-motile and motile forms of what appeared to be *Chromatium*, *Thiothece* and *Thiospirillum* sulfur bacteria, in descending order of abundance. Unidentified rods and spheres were very common. |
| | | Algae in 001 were relatively uncommon, with *Chlamydomonas* and *Chlorella* present. In 003, *Phacus* and *Chlamydomonas* were common, and *Chlorella* and *Ankistrodesmus* rare. |
| | | Flagellated protozoans were common in both samples. |
| | | Fine organic particles were common, but no wood or paper were observed. |
| | | The Clark Fork at Huson contained primarily periphytic algae (diatoms, filamentous greens and blue-greens). None of the forms common to Champion wastewater were observed. Bacteria were very rare, while much inorganic sediment was present. Nothing visually attributable to Champion wastewater was identified. |
| 6/18/85 | 003 | Color and odor was typical of Champion effluent. |
| | | The biota was dominated by purple sulfur bacteria *Chromatium*, *Thiothece* and *Thiospirillum*, colorless sulfur bacterium *Macromonas*, and many very small unidentified spherical bacteria. |
| | | *Phacus* and *Chlamydomonas* were again the common algae, with *Ankistrodesmus* and diatoms rare. |

Table 7. Continued

| Date Collected | Discharge Number | Analysis |
|---|---|---|
| | | Flagellated and ciliated protozoans and planktonic rotifers were common. |
| | | Fine organic particles were common, but no wood or paper fibers were observed. |
| 7/29/85 | 002 | The sample appeared to be darker brown in color than previous Champion effluent samples, and didn't have as strong a sulfurous odor. |
| | | The flora was largely dominated by bacteria, with much fewer algae than before. What appeared to be the sulfur bacteria *Thiothece*, *Chromatium*, and *Macromonas*, in decreasing order of abundance, were most obvious. Many other less conspicuous forms were present in great numbers. |
| | | Algae present included *Oscillatoria*, *Chlamydomonas* and possibly *Oocystis*, all uncommon to rare. |
| | | Protozoans were noted, but were relatively uncommon. |
| | | Particulate organic matter was spare, and no paper or wood "fibers" were seen. |

## FISH FLESH TASTE AND ODOR EVALUATIONS

### Rationale

In order to address citizen complaints of catches of off-flavor fish in the Clark Fork below the Champion mill during periods of direct discharge, several standardized flavor and odor tests using rainbow trout were conducted during the study period.

### Methods

The first test utilized hatchery-reared rainbow trout brood stock which had been exposed in aquaria to river water dilutions of Champion effluent ranging from 200:1 (the theoretical maximum instream concentration of wastewater after mixing) to 10:1. Following the exposure period, fish were baked and rated for off-odor and off-flavor by a panel of 20 judges at Oregon State University.

The second test consisted of an identical evaluation of resident Clark Fork rainbow trout collected from several locations above and below Champion's direct discharge.

### Results

The results and more detailed methods and descriptions of the two flavor evaluation tests are given in the following pages.

Champion

January 30, 1985

Mr. Glenn Phillips
Water Quality Bureau - DHES
Cogswell Building
Helena, MT 59620

Dear Mr. Phillips:

Enclosed are two reports concerning the fish taste study which was run in October and November on the Champion Frenchtown Mill effluent. This study completes the first of the two fish flavor studies required by Champion's MPDES permit.

The first of the enclosed reports is by Dr. Vance Thurston of Montana State University and details the procedures used to expose rainbow trout to the mill effluent. The mill effluent used was the treated waste water that was being discharged to the river. The concentrations of effluent used for these flavor tests were 1/10, 1/50, 1/100, and 1/200. The mill effluent is discharged to the river at concentrations less than the 1/200 dilution. The only time a 1/200 would be approached would be at times during the high river flows in the spring.

The second report is the one submitted by Dr. Mina McDaniel of Oregon State University with the results and data from the fish tasting panels. Generally, the results indicate that effluent at 1/100 and 1/200 concentrations do not impair the flavor or odor of fish.

If you have any questions concerning these reports or the tests, please contact me.

Sincerely,

Bill Henderson
Bill Henderson
Environmental Supervisor

sp

Enclosure

c: Potts
Weeks
Clem
Steve Pilcher

[illegible]
JAN 31
MONTANA DEPT. OF HEALTH
& ENV. SCIENCES
WATER QUALITY BUREAU

1 November 1984

# PROCEDURES USED DURING LABORATORY EXPOSURE OF RAINBOW TROUT TO KRAFT MILL WASTE WATER, OCTOBER 1984

A REPORT TO CHAMPION INTERNATIONAL CORPORATION,
FRENCHTOWN MILL, MISSOULA, MONTANA

Robert V. Thurston

Fisheries Bioassay Laboratory
Montana State University
Bozeman, Montana 59717

# INTRODUCTION AND BACKGROUND

This report covers the background of, and procedures used during, exposure tests at Fisheries Bioassay Laboratory (FBL), Montana State University (MSU), of rainbow trout (Salmo gairdneri) to Kraft mill waste water received in October 1984 from the Frenchtown, Montana, paper mill of the Champion International Corporation.

Robert V. Thurston, Director of FBL, was contacted by telephone by Dr. Glenn Phillips, Montana Fish, Game, and Parks, in early summer 1984. Phillips asked Thurston if FBL would be able to conduct exposure tests for Champion; if so, contact should be made with Mr. Bill Henderson at Champion. In a subsequent series of telephone conversations during June - October 1984 with Phillips, Henderson, Mr. Larry Weeks (Champion), and eventually Dr. Mina McDaniels and Professor Jerry Starks (both of the Department of Food Science and Technology, Oregon State University, Corvallis), the following test procedure was decided upon.

## Basic Research Plan

Fish would be exposed at FBL to four different dilutions of Kraft mill waste water for a 48-hour period. The exposure would be a modified static test, with water changed at ~12-hour intervals. The exposure concentration would be 1 part waste water in 10 parts solution, 1 in 50, 1 in 100, and 1 in 200, in addition to a control group of fish exposed only to dilution water. Twice as many control fish would be needed as the number of fish tested at each exposure concentration. During the exposure period at FBL, measurements would be made of temperature and dissolved oxygen (D.O.) concentrations in each exposure tank.

The range of exposure concentrations was chosen by the following rationale: the "worst possible case" of Kraft mill waste water concentration, after mixing of the Frenchtown mill effluent into the Clark Fork River, was reported to be 0.5% (Henderson); concentrations of Kraft mill waste water in the range 1-10% (v/v) have been reported to induce off-flavor to fishes (Persson 1984).

The dilution water for the solution would be that available to FBL from a ground spring source, characteristics of which are listed in Table 1. For comparison, characteristics of the Clark Fork River above the Frenchtown mill, as reported by U.S. Geological Survey (1984) are provided in Table 2. The Champion Paper Company discharge point into the Clark Fork is approximately 11 km downstream from the Geological Survey monitoring station.

After exposure at FBL, fish would have their heads removed, be gutted and scaled, individually packaged in aluminum foil, and immediately preserved by freezing. Fish would subsequently be packaged in dry ice and shipped by air carrier to Oregon State University (OSU) where they would be prepared for and tasted by duplicate flavor-test panels.

Preliminary Tests

In conversation with McDaniels and Starks, it was determined that the ideal size fish for flavor test preparation at OSU would be fish in the 2-3 lb. (1-1.5 kg) range. Mature rainbow trout (Winthrop strain) of this size were obtained from the Fish Technology Center, U.S. Fish and Wildlife Service, Bozeman, and transferred to FBL on 27 September 1984. These fish were maintained in circular (1.2 m diameter) holding tanks with a water volume of 600 liters.

Table 1. Characteristics of dilution water at FBL. (Values are mg/liter unless noted otherwise.)

| | | | |
|---|---|---|---|
| Al | <0.02 | Mo | <0.05 |
| Ba | 0.031 | Ni | <0.05 |
| Be | <0.002 | P | <1 |
| B | <0.01 | K | 0.48 |
| Cd | <0.005 | Si | 0.3 |
| Ca | 46 | Na | 0.6 |
| Cl | <1 | Sr | <0.05 |
| Cr | <0.1 | Zn | 0.01 |
| Cu | <0.002 | $PO_3^{3-}$ | 0.05 |
| F | 0.35 | $SO_4^{2-}$ | 17 |
| Fe | <0.004 | | |
| Pb | <0.01 | Total organic carbon | 3.3 |
| Mg | 9.8 | Specific equivalent conductance, siemens 25 C | 340 |
| Mn | 0.006 | Turbidity, nephelometric turbidity units | 1.6 |
| Hg | <0.00005 | | |

Table 2. Characteristics of Clark Fork River water above the Champion mill at Frenchtown, Montana.[a] (All values reported are mg/liter unless otherwise specified.)

| Variable | Range |
|---|---|
| Temperature | 0.0-22.5C |
| pH | 7.8-8.4 |
| Dissolved oxygen | 8.8-13.0 |
| S.E.C. (umhos, 25C) | 118-278 |
| Alkalinity (as $CaCO_3$) | 55-117 |
| Hardness (as $CaCO_3$) | 58-130 |
| Ca | 16-38 |
| Mg | 4.3-9.6 |
| Na | 2.6-7.4 |
| K | 1.1-3.3 |
| $SO_4^{2-}$ | 9.5-36 |
| P (Total) | 0.03-0.12 |
| $Cl^-$ | 0.9-3.2 |
| $NH_3$-N | 0.12-0.59 |

[a] Source U.S. Geological Survey (1984). Range of values reported are those for the water year 1983 (October 1982-September 1983). See reference source for more information.

During 2-4 October 1984 preliminary tests were conducted at FBL to determine the rate of oxygen consumption of these fish under a static (non flow-through) test condition. The actual weight of the fish tested were in the 1.0-1.2 kg range. It was determined that with six fish of this size in 600 liters of water in the test tanks to be used, the D.O. loss over a 4-hour period was approximately 0.2 mg/liter/fish/hr, although this rate decreased after 4 hours to as low as 0.1 mg/liter/fish/hr. It was further determined that these fish could survive for periods up to 12 hours at concentrations as low as 2-3 mg/liter D.O.

The oxygen demand of the Kraft mill waste water itself was approximated by a test conducted by Champion personnel in Frenchtown, and reportd by Weeks to Thurston on 19 September. In this test the D.O. concentration of available tap water was measured, and using this as dilution water, a 10% solution of mill waste water was prepared. The D.O. concentration of the mixture was measured at 1-hour intervals for 11 hours; results are reported in Table 3. The D.O. decrease at 1 hour is attributed primarily to the mixture of the mill waste water at essentially zero D.O. concentration with the tap water. The drop in concentration over the next 10 hours was approximately 0.1 mg/liter/hour. This was considered to be of minimal consideration to the projected D.O. demand by the test fish.

Initially, we preferred not to aerate the exposure solutions during test because of the unknown amount of volatiles in the Kraft mill waste water. Under the modified static test regime proposed, however, the D.O. concentrations could approach dangerously low levels, causing metabolic stress to the fish and possibly death. The alternatives were to change the test concentrations at more frequent intervals (3 or 4 hours), or changing to a flow-through test design. Either alternative would have markedly

Table 3. Oxygen demand of Kraft mill waste water, 10% solution in tap water (Test conducted by Champion personnel at Frenchtown.)

| Elapsed time, hours | Dissolved oxygen, mg/liter |
|---|---|
| 0 | 8.0[a] |
| 1 | 7.5 |
| 2 | 7.5 |
| 3 | 7.6 |
| 4 | 7.4 |
| 5 | _ [b] |
| 6 | 7.2 |
| 7 | 7.1 |
| 8 | 6.9 |
| 9 | 6.6 |
| 10 | 6.6 |
| 11 | 6.4 |

[a] D.O. concentration in tap water prior to mixing.

[b] Not measured

increased the amount of Kraft mill waste water to be transported from Frenchtown to Bozeman. A decision was made to aerate the solutions to be tested, based on the test protocol for Kraft mill waste water reported by Shumway and Palensky (1973). We also elected to maintain the control fish under flow-through conditions, primarily because we wanted the control fish to be under the least possible stress conditions, including non-handling during test.

The number of fish to be tested at each exposure concentration was predicated on the amount of cooked meat required for the flavor-test panels; there were to be two panels, each of 20 persons, each person requiring 2 oz. of cooked meat for sampling; a total of 80 oz. (2.3 kg) of cooked meat would be required from fish from each exposure concentration. To determine the number of test fish required, we chose two fish from the test pool, one of these visually observed to be slightly larger than the mean, and one slightly smaller. These were killed, weighed, prepared for cooling, weighed again, wrapped in aluminum foil, and baked at 375 F for 25-30 minutes (baking procedure from Starks, OSU). Their carcasses were picked clean of flesh, and weighed again. Results of this sub-test are reported in Table 4. From this test it was determined that slightly better than 50% of the wet weight of the test fish would be meat available to the flavor-test panel. To provide the necessary amount of cooked meat, ~5 kg of fish would need to be tested at each concentration, or a minimum of 3-4 fish of the size available (1.0-1.2 kg). We elected to test eight fish at each concentration (and twice as many control fish) on the chance there might be some mortality during test.

Table 4. Results of sub-test to determine percent edible meat composition of test fish.

| | Fish #1 | Fish #2 |
|---|---|---|
| Whole fish, wet weight | 1530 g | 1216 |
| Dressed fish | 1056 | 844 |
| Carcass after cooking | 228 | 210 |
| Net weight of cooked flesh | 828 | 634 |
| Cooked meat/whole fish | 54% | 52% |

# TEST PROCEDURES

Three days prior to test (5 October 1984) approximately 100 fish were transferred from the FTC outdoor raceway to the tanks to be used during the exposure test at FBL. On 8 October these fish were sorted and uniform size fish (1.0-1.3 kg) were retained for test. Eight fish were placed in four test tanks, and 22 fish in the control tank. All fish were maintained under flow-through conditions for the next day. On the evening of 8 October approximately 100 gallons (20 5-gallon pails) of Kraft mill waste water were brought to FBL from Frenchtown by Henderson. This waste water was collected earlier that day from the effluent being discharged from outfall 003 at the Frenchtown mill (Henderson).

At 0900 on 9 October the test was started. Three liters of waste were mixed with ~597 liters of dilution water in one of the test tanks (1/200 concentration). The first group of eight fish was transferred to this tank. The tank from which these fish had been taken was drained, and prepared with 6 liters of waste water and ~594 liters of dilution water (1/100 concentration), mixed, and the next group of eight fish was transferred to this tank. This procedure was repeated two more times, transferring eight fish to each of 1/50 and 1/10 concentration mixtures. The mixing of test solution and transferring of fish required approximately 1 hour, so the actual start-of-test time for the fish at the highest concentration (1/10) was 1 hour later than that for those fish at the lowest concentration (1/200). Incoming water to the test tanks was shut off at the time of mixing the test concentration, and a dual-piston air pump with two air stones was used to provide air to each test tank. The control fish were maintained in a single tank throughout the test under flow-through conditions. Immediately after all fish were under test, D.O.

and temperature was measured in each tank; these were measured again at 1440 hours (7.6 hours into test) as a check to ensure that adequate D.O. concentrations were being maintained, and the test was going according to plan. At this time no fish were observed to be under stress, although because of the reduced transparency of the solutions it was difficult to see the fish at the 1/50 test concentration and virtually impossible to see the fish at the 1/10 test concentration.

At 11 hours into test, D.O. and temperature were again measured in each tank, and the rotation of the test fish into freshly prepared test solutions was again started, beginning with the fish at the 1/200 test concentration. These fish were transferred to a fresh 1/200 test concentration in a tank which had been thoroughly cleaned. A fresh 1/100 test concentration was mixed in the tank which had had the 1/200 test concentration, and the fish exposed to the 1/100 test concentration were transferred to it. The fish at 1/50 test concentration were transferred to the tank which previously had contained the 1/100 test concentration, and the fish at 1/10 test concentration were transferred to the tank which previously had contained the 1/50 test concentration. In each case, the fresh test concentrations were mixed in a tank which had previously been used for the next lower test concentration. After rotation of all test fish, the tank which had contained the 1/10 dilution was thoroughly rinsed, and purged of carry-over solution by flushing with fresh dilution water for the next 12-hour period. Condition of the fish at the 1/50 and 1/10 test concentration was easily observed by draining the tanks to a low level before the fish were transferred; none appeared under stress. This same transfer procedure was again followed at approximately 24 and 36 hours into test, always in the same order. The process of mixing solutions and transferring fish required approximately 1 hour each time. Results of the D.O. and temperature measurements, before and after transfer, and again just prior to completion of the test, are reported in Table 5. There was no correlation between either test solution concentration or air pump efficiency and D.O. concentrations.

At 0900 on 11 October (48 hours into test) the sacrificing of test fish was started, beginning with the fish at the 1/200 test concentration. Each fish was killed by a sharp blow to the head, the head and caudal fin removed, the body gutted and scaled, and packaged in heavy duty aluminum foil. It required approximately 45 minutes to prepare all fish at each concentration; the last lot of test fish (1/10 concentration) were killed at 1115 hours and packaged by 1200 hours. The total exposure time of the 1/10 concentration fish was, therefore, ~49 hours. The control fish (16 fish total) were prepared and packaged by 1340 hours. At the time each fish was cleaned, its sex was determined; the breakdown by concentration and sex is reported in Table 6.

Table 5. Results of D.O. and temperature measurements during 48-hour exposure period.

| Test dilution concentration | Time into test (hours) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1.3 | 7.6 | 11.0 | 12.1 | 23.5 | 24.7 | 35.0 | 36.2 | 47.8 | Mean (Range) |
| | Dissolved oxygen (mg/liter) | | | | | | | | | |
| Control | 8.6 | 8.7 | 9.0 | - | 9.0 | - | 9.0 | - | 8.6 | 8.8 (8.6-9.0) |
| 1/200 | 5.9 | 7.0 | 6.8 | 8.0 | 6.1 | 7.8 | 5.6 | 8.0 | 4.3 | 6.6 (4.3-8.0) |
| 1/100 | 7.7 | 6.6 | 6.7 | 8.5 | 6.7 | 8.6 | 7.1 | 9.2 | 6.3 | 7.5 (6.3-9.2) |
| 1/50 | 8.3 | 7.0 | 6.1 | 9.1 | 5.3 | 9.6 | 7.0 | 9.6 | 6.2 | 7.6 (5.3-9.6) |
| 1/10 | 8.0 | 6.7 | 6.7 | 8.6 | 6.1 | 8.7 | 5.6 | 9.0 | 6.4 | 7.3 (5.6-9.0) |
| | Temperature (°C) | | | | | | | | | |
| Control | 7.7 | 7.9 | 7.8 | 7.9 | 7.7 | - | 7.8 | - | 7.9 | 7.8 (7.7-7.9) |
| 1/200 | 8.1 | 9.3 | 10.4 | 8.2 | 10.6 | 8.3 | 10.7 | 8.4 | 10.8 | 9.4 (8.1-10.8) |
| 1/100 | 8.1 | 9.3 | 10.4 | 8.3 | 10.4 | 8.3 | 10.3 | 8.4 | 11.0 | 9.4 (8.1-11.0) |
| 1/50 | 8.1 | 9.4 | 10.5 | 8.3 | 10.5 | 8.4 | 10.3 | 8.4 | 10.7 | 9.4 (8.1-10.7) |
| 1/10 | 8.7 | 10.0 | 11.1 | 9.1 | 11.3 | 8.9 | 10.7 | 9.1 | 11.0 | 10.0 (8.7-11.3) |

Table 6. Sex of test fish by test concentration.

| Concentration | No. of Fish | |
|---|---|---|
| | Males | Females |
| Control | 8 | 8 |
| 1/200 | 5 | 3 |
| 1/100 | 3 | 5 |
| 1/50 | 2 | 6 |
| 1/10 | 4 | 4 |

## STORAGE AND SHIPPING OF FISH AFTER EXPOSURE

After each fish carcass was packaged in aluminum foil, these packages were combined in plastic bags (four fish/bag), the bags tagged to show exposure concentration, and refrigerated. The complete set of test and control fish were then transferred to a freezer in Cooley Laboratory on the MSU campus, where they were stored from 1500 hours on 11 October until 1600 hours on 15 October. At that time the plastic bags were packaged in two styrofoam boxes, six bags/box, each with ~10 kg of dry ice, and delivered by 1700 hours to Federal Express at Gallatin Field, Bozeman, for shipment to OSU. They were reported by Starks to have been received at OSU prior to 1500 local time, in frozen condition, and a residue of dry ice still in each container.

## SUPPLEMENTAL ACTION AFTER INITIAL FLAVOR TESTS

On 24 October it was reported to Thurston by McDaniels that the flavor tests (2 panels) had been conducted on 19 October. Initial analysis of the results of the flavor test indicated that one panel found no significant difference in off-flavor among the test and control groups. The other panel, however, had detected slight off-flavor of both the fish exposed at 1/10 dilution and the control fish. McDaniels also reported that only half the fish provided were required for the flavor test.

After discussion between McDaniels and Thurston, and consultation with Henderson, it was decided to re-run the flavor test at OSU during the week of 29 October, using the remaining fish, but this time to include a second control group of fish; this group to be fish from the pool still at FTC. On 25 October between 0900 and 1030 hours four fish from the FTC pool were sacrificed, cleaned as before, and packaged for shipment to OSU. Two males and two females were selected and packaged separately. These fish were kept cool and placed in a freezer at Cooley Laboratory by 1100 hours, packed in a styrofoam container with ~10 kg dry ice at 1630 hours, and picked up by Federal Express at 1700 hours for over-night shipment to OSU. It was reported to Thurston at 1700 hours on 26 October that the fish had been received earlier in the day at OSU.

# OBSERVATIONS ON POTENTIAL FOR ACUTE TOXICITY OF THE KRAFT MILL WASTE WATER TESTED

Although the exposure regime employed was intended for the purpose stated in the Backgound section above, i.e., whether bioconcentration of components in Kraft mill waste water by the test fish might result in flavor impairment, there is also an observation that can be made regarding the relative toxicity of the waste water. It's acute toxicty was not tested, but a conclusion that can be drawn is that under the test conditions, and for the test fish employed, a 10% concentration (v/v) of the Kraft mill waste water was not acutely toxic during a 48-hour test period. Considering the overall vigor of the fish in the 10% concentration test tank at the close of the 48-hour test period, presumably these fish could have endured exposure for a longer period, the length of which is not known. There were no observable signs of impairment resulting from stress to the fish at any of the dilution concentrations, other than those usually observed for this size trout maintained in a relatively confined test environment. Neither was there any visually apparent correlation between exposure concentration and overall physical appearance or behaviour.

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U.S. Geological Survey. 1984. Water resources data, Montana, water year 1983. Volume 2. Columbia River basin. Water-Data Report MT-83-2, U.S. Geological Survey, Helena, Montana. 192 p.

Sensory Science Laboratory
Department of Food Science and
Technology
Oregon State University
Submitted by: Dr. Mina R. McDaniel
November 15, 1984

# FLAVOR EVALUATION REPORT

PRODUCT: Trout

SUBMITTED TO: Champion International

DATES TESTED: October 19, 1984 and November 2, 1984

TEST NUMBERS: S204-84 (2 replicates), S220-84 (2 replicates)

PANEL: Twenty experienced judges made up of university staff and students.

BALLOT: Off-odor and off-flavor rated on a 9-point intensity scale (1, no off-odor to 9, extreme off-odor) and overall acceptability rated on a 9-point scale (9, extremely desirable to 1, extremely undesirable).

SAMPLES: Control samples, plus samples exposed to Kraft Mill Effluent at dilutions of 1/10, 1/50, 1/100, 1/200.

## PROCEDURES:

The fish were frozen when they arrived. They were thawed overnight at room temperature. The fish were placed on aluminum foil covered broiler pans and baked 35 minutes at 375°F. The baked fish was skinned, boned and the flesh was flaked and thoroughly mixed. The flesh was held in the top of a double boiler over hot water until served. The second trout test was run with the original control and a new control.

The same 20 judges served on each replicate test. However, some of the judges were different for the second set of tests. The judges were not screened for tasting acuity but were experienced in the type of flavor evaluation testing and were knowledgeable regarding quality trout aroma and flavor.

## RESULTS:

The following tables give the sample mean scores and the treatment Least Significant Differences (LSD) at the five and one percent levels. These data were analyzed by a three factor analysis of variance (copies attached).

RESULTS: (cont.)

## TABLE I

### Trout Test #1

Two Replications Analyzed Together

| | Off-odor | Off-flavor | Overall Desirability |
|---|---|---|---|
| C | $2.7^{a*}$ | $4.03^{b}$ | $5.45^{a}$ |
| 1/10 | $3.28^{b}$ | $3.98^{b}$ | $4.95^{a}$ |
| 1/50 | $2.55^{a}$ | $2.68^{a}$ | $6.43^{b}$ |
| 1/100 | $2.53^{a}$ | $2.58^{a}$ | $6.6^{b}$ |
| 1/200 | $2.28^{a}$ | $2.83^{a}$ | $6.38^{b}$ |
| LSD<br>(.05) | 0.58 | 0.76 | 0.72 |
| (.01) | 0.77 | 0.99 | 0.96 |

---

## TABLE II

### Trout Test #2

Two Replications Analyzed Together

| | Off-odor | Off-flavor | Overall Desirability |
|---|---|---|---|
| $C_1$ (original) | $2.43^{a}$ | $2.43^{a}$ | $5.88^{c}$ |
| $C_2$ (new) | $3.40^{b}$ | $4.16^{b}$ | $4.82^{b}$ |
| 1/10 | $4.03^{b}$ | $5.18^{c}$ | $4.10^{a}$ |
| 1/50 | $4.18^{b}$ | $4.58^{b}$ | $4.30^{ab}$ |
| 1/100 | $2.18^{a}$ | $2.18^{a}$ | $6.48^{cd}$ |
| 1/200 | $1.95^{a}$ | $1.90^{a}$ | $6.55^{d}$ |
| LSD<br>(.05) | 0.61 | 0.65 | 0.67 |
| (.01) | 0.80 | 0.86 | 0.89 |

* a,b,c,d Any mean scores in any one column with the same superscripts are not significantly different from each other.

Table I contains the sample mean scores from the first two replicates. For all three attributes, the 1/10 sample was significantly different from the other treated samples, and the other treated samples were not significantly different from each other. The 1/10 sample was significantly higher in off-odor and off-flavor, and it was significantly lower in overall desirability than the other treated samples. In off-odor, the panel judged the control to be significantly lower in off-odor than the 1/10 sample, however it was judged to be not significantly different from the 1/10 sample in off-flavor and overall desirability.

Because of the unexpected flavor and desirability rating of the control, another test was run including the original control and treated samples which were held at -10°C for about 15 days, and a new control supplied by Montana State University.

Table II contains the sample mean scores from the second two replicates. In the second series of tests more differences among treatments were noted by the panel. In off-odor the original control was not different from the 1/100 and 1/200 samples. In off-flavor, the original control was again not significantly different from 1/100 and 1/200 samples. The new control was rated not significantly different from the 1/50 sample. Neither the new control nor the 1/50 sample was as high in off-flavor as the 1/10 sample. In overall desirability samples 1/10 and 1/50 were rated the lowest and were not significantly different from each other. The 1/100 and 1/200 samples were rated as most desirable, both being more desirable than the new control.

It is not apparent why the controls in test I and in test II are being rated high in off-odor and/or flavor. In testing fish it is usually recommended to do many replicates (as many as six) in order to compensate for the normal variation from fish to fish. This may have been a problem here. Perhaps the odor and flavor of fish is improved by low levels of Kraft Mill effluent.

Mina R. McDaniel

Dr. Mina R. McDaniel
Assistant Professor

Attachments

MRM/tlm

ECEIVED

JAN 31 1985

MONTANA DEPT. OF HEALTH
& ENV. SCIENCES
ATER QUALITY BURE

[illegible]
[illegible] Montana [illegible]
406 626-4451

**Champion**
Champion International Corporation

November 21, 1985

Glenn Phillips
Water Quality Bureau
Cogswell Building
Helena, MT 59620

Dear Glenn:

Enclosed please find a copy of the second fish taste test results from Oregon State University. The fish tested were taken from the Clark Fork River in early October 1985. According to Ron Stone of the Missoula office of Fish, Wildlife & Parks, there were ten mature fish for each of the "above" and "below" samples. The "above" samples were fish taken from the river from Harper's Bridge to approximately 2 miles upstream. The "below" samples were taken from the river between outfall 003 and Six-mile Creek.

If I can be of further assistance with this test, please let me know.

Sincerely,

Bill Henderson

Bill Henderson
Environmental Supervisor

kj

c: Potts
Weeks
Gary Ingman, WQB

Oregon State University
Department of Food Science and Technology
Sensory Science Laboratory
Submitted by: Mina R. McDaniel and Lee Ann Henderson

Department of
Food Science
and Technology
College of
Agricultural Sciences

Oregon State University

Corvallis, Oregon 97331-6602 (503) 754-4636

DATE: November 12, 1985

# FLAVOR EVALUATION REPORT

PRODUCT: Trout

SUBMITTED BY: Glenn Phillips, Montana Fish and Wildlife

DATE TESTED: 10/15/85

TEST NUMBER : S235-85

PANEL: 20 University staff and students

BALLOT: nine-point intensity for off odor, off flavor and nine-point overall desirability

SAMPLES: above Kraft mill
below Kraft mill

PROCEDURE:

The fish were received in early October and were placed in the freezer until October 13 when they were placed in a 40°F cold room for 48 hours. The day of the test (10/15/85), the samples were rinsed in cold water and baked at 350°F in foil lined and covered trays for 35-45 minutes. When the samples had finished baking, the meat was separated from the skin and bones and placed in the top portion of a double boiler, hot water in the bottom portion kept the samples at serving temperature, 100°F.

Approximately one ounce portions were served in plastic portion cups coded with 3-digit random numbers. Placement of the samples on the serving trays were randomized and each panelist did replicate tests. The panelists were seated in individual testing booths under red lighting.

PROCEDURE (cont.):

The judges were asked to rate the two coded samples for off odor and off flavor using a nine point intensity scale with 1 being none and 9 being extreme. The samples were also rated for overall desirability on a nine point desirability scale with 9 being extremely desirable to 1 extremely undesirable.

The judges were volunteers and chosen solely on availability, but were experienced in serving on flavor evaluation panels.

RESULTS:

The following table shows the sample mean scores and the Least Significant Differences (LSD).

TROUT

| SAMPLES | OFF ODOR | OFF FLAVOR | OVERALL DESIRABILITY |
|---|---|---|---|
| Above | $2.08^a$ | $2.38^a$ | $6.20^a$ |
| Below | $2.40^a$ | $2.50^a$ | $6.10^a$ |
| LSD (.05) | 0.55 | 0.61 | 0.55 |
| (.01) | 0.73 | 0.82 | 0.73 |

NOTES: Same letter superscripts indicate no significant difference at the 5 level.

Off odor and off flavor intensity scales: 1, none to 9, extreme; desirability scale: 9, extremely desirable to 1, extremely undesirable.

There were no significant differences between the samples for off odor, off flavor, or overall desirability. Comments on the samples and a sample ballot are attached.

Mina R McDaniel

Mina R. McDaniel, Ph.D.
Assistant Professor

Lee Ann Henderson
Research Assistant

Attachments

MRM/LAH/tlm

Attachment
November 15, 1985

# MONTANA TROUT
October 15, 1985

549 & 309 (below)

- largely desirable taste
- great, no smell and good taste
- sweeter
- tuna like aroma
- tuna like
- tasted like cahhed fish--similar to the difference between fresh vs. canned salmon
- tuna type flavor
- metallic taste

984 & 579 (above)

- slightly desirable taste
- tastes like chicken
- dry
- strange after taste
- fish type odor--strong
- metallic taste

NAME ________________

DATE ________________

[illegible] BALLOT

Please evaluate each sample for degree of off-odor, off-flavor, fishiness and overall desirability.

OFF-ODOR

___ none

___ just detectable

___ slight

___ [illegible]

___ moderate

[illegible]

[illegible]

[illegible]

[illegible]

OFF-FLAVOR

___ none

___ just detectable

___ slight

___ slight to moderate

___ [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

OVERALL DESIRABILITY

___ ~~none~~ extremely desirable

___ ~~just detectable~~ largely desirable

___ ~~slight~~ moderately desirable

___ ~~slight to moderate~~ slightly desirable

___ ~~moderate~~ neither/nor

___ slightly undesirable

___ moderately undesirable

___ largely undesirable

___ extremely undesirable

```
******************
*                *
* [illegible]    *
*                *
******************

COMPANY IS MONTANA DEPT. OF FISHERIES

DATE OF TEST WAS 10-13-85

PRODUCT TESTED WAS TROUT

TEST CONDUCTED WAS OFF ODOR


*****************[illegible]*****************

[illegible]

*****************************************
```

[illegible]

```
            *****************
            *               *
            * OSU FLAVORIUM *
            *               *
            *****************


        COMPANY IS MONTANA DEPT. OF FISHERIES

        DATE OF TEST WAS 10-15-85

        PRODUCT TESTED WAS TROUT

        TEST CONDUCTED WAS OFF FLAVOR


**************ANOVA TABLE****************
   SOURCE    DF       SS        MS      F
-----------------------------------------

  PANELIST  19    154.94    8.15    4.44

  TRT        1      .31      .31     .17

  P*T       19    44.94     2.37    1.29

  ERROR     40    73.5     1.84

  TOTAL     79    273.69
*****************************************


            TREATMENT      MEAN
            -----------------
                1         2.5
                2         2.375


            LSD AT 5% = .612999651

            LSD AT 1% = .820163808
```

```
                 *****************
                 *               *
                 * OSU FLAVORIUM *
                 *               *
                 *****************

              COMPANY IS MONTANA DEPT. OF FISHERIES

              DATE OF TEST WAS 10-15-85

              PRODUCT TESTED WAS TROUT

              TEST CONDUCTED WAS OVERALL DESIRABILITY


          **************ANOVA TABLE****************

            SOURCE    DF       SS        MS      F
          ------------------------------------------

           PANELIST  19    183.7    9.67    6.55

           TRT         1    .2    .2    .14

           P*T        19    37.3    1.96    1.33

           ERROR     40    59    1.48

           TOTAL     79    280.2

          ******************************************


               TREATMENT      MEAN
               ------------------
                   1          6.1
                   2          6.2


               LSD AT 5% = .549771438

               LSD AT 1% = .735567525
```

# SUMMARY

The findings of these investigations indicate that aesthetic problems did occur in the lower Clark Fork in 1984 and 1985 and probably resulted in a somewhat diminished recreational potential. Some of the problems--like the high river color in several localized seepage areas--were definitely linked to the Champion wastewater disposal system: Others--like the accumulations of river foam below Huson and an apparent increase in river organic suspended solids levels--were possibly associated with the Champion discharges. Other significant aesthetic problems clearly not associated with Champion were documented and included:

1) Unnatural increases in river turbidity due to the annual operational drawdown of Milltown Dam,
2) A localized reduction in aesthetics in the mixing zone for the Missoula WWTP discharge,
3) A foam problem in the lower Bitterroot and
4) Unnatural fluctuations in river and reservoir water levels due to the operation of hydroelectric facilities on the lower Clark Fork and Flathead Rivers.

Reported problems that can now be dismissed include the presence of wood fiber deposits in and along the river and, probably, the possibility of fish tainting due to the Champion discharge. However, it would be wise to rerun the test using resident rainbow trout during the high Champion wastewater discharge period of spring or early summer.

It seems likely that the Champion wastewater is responsible for the increased river foam because of its proven foaming tendency and the known presence of surfactants. At this time, the foam organic analysis results have not been received. They may provide a connection between the wastewater and downstream foam.

Further evaluations of these aesthetic monitoring data are included in the Champion draft EIS.

# B. ALGAL BIOASSAYS

# RESULTS OF ALGAL ASSAYS PERFORMED ON WATERS COLLECTED FROM THE LOWER CLARK FORK RIVER SYSTEM AT STATIONS BELOW MILLTOWN DAM TO BELOW NOXON DAM

## Report I: December 10-14, 1984 Sampling

by
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U.S. Environmental Protection Agency
Corvallis Environmental Research Laboratory
Hazardous Waste and Water Branch
Hazardous Waste Assessment Team
200 S.W. 35th Street
Corvallis, Oregon 97333

## INTRODUCTION

A large amount of public concern has been expressed over the general health of the lower Clark Fork River system. The proposed modification of the existing wastewater discharge permit for the Champion International paper mill at Frenchtown has generated much of this concern. Other sources of wastewater, namely the City of Missoula wastewater treatment plant and historic metals deposits originating upstream from Milltown Dam, have also been mentioned as possible sources of stress on the river (Montana, 1984).

The *Selenastrum capricornutum* algal assays performed during this study were undertaken to fulfill a request for technical assistance from the Montana Water Quality Bureau through the US EPA Region VIII Water Management Branch staff in Denver, CO. The Montana Department of Health and Environmental Services has a lower Clark Fork River Monitoring Plan. Data gathered from these assays will be used in conjunction with other data collected under this monitoring plan to define existing conditions in the Lower Clark Fork River system.

## METHODS

Water was collected, as surface grab samples, from nine sites along the Clark Fork River (Table 1) by Mr. Gary Ingman a biologist with the Department of Health and Environmental Sciences, State of Montana. River water collected at each site was composited in a large container and mixed well. Water from the large container was subsampled for algal assay by the US EPA Corvallis Environmental Research Laboratory, OR. (CERL) and nutrient and metals analysis by the State of Montana. The samples were shipped, in autoclavable polypropylene bottles, through the

TABLE I. Identification of Clark Fork River sampling stations showing both Montana and EPA site identification codes.

CLARK FORK RIVER

SITE IDENTIFICATION

| MT | EPA | |
|---|---|---|
| 4 | 10 | Below Milltown Dam |
| 6 | 11 | Above Missoula WWTP |
| 11 | 12 | At Harper Bridge (above Champion) |
| 15 | 13 | At Huson (below Champion) |
| 20 | 14 | At Superior |
| 22 | 15 | Above Flathead River confluence |
| 25 | 16 | Above Thompson Falls Reservoir |
| 27 | 17 | Below Thompson Falls Reservoir |
| 29 | 18 | Below Noxon Dam |

US Postal Service. They were received within 3 days of sampling.

Algal assays were performed according to the methods outlined in the Selenastrum capricornutum Algal Assay Bottle Test (Miller, Greene and Shiroyama, 1978). The water samples were pretreated by autoclaving followed by filtration through a 0.45 micrometer filter. Test flasks were dispensed in triplicate, inoculated with a final concentration of 1000 cells/ml and cultured for 14-days. Results were reported as calculated mg dry weight S. capricornutum/liter.

The Montana Water Quality Bureau's data sheets for chemical analysis of the Harper Bridge (Site 12) and Huson (Site 13) samples indicate that they contained bits of scoured algal particles and debris. When the samples were received at CERL they were autoclaved in their shipping containers. These two samples, therefore, may have demonstrated greater algal growth potential than that which would have been found in the overlying waters. The degree of bias caused by contamination of these samples is unknown.

All applicable QA/QC procedures outlined in the HMAT quality assurance plan (US EPA, 1984) were strictly adhered to.

## RESULTS AND DISCUSSION

The algal assay mean maximum yield, standard deviation and coefficient of variation is shown in Table II for the controls cultures as well as those spiked with nutrient and chelator (EDTA) additions. The control yields from the nine sites ranged from 0.04 to 4.73 mg dry weight/liter. Test flasks spiked with 0.05 mg P/liter produced algal yields that were from 3 to 99 times greater than those found in their concomitant control cultures. The addition of a combined nitrogen plus phosphorus spike also increased yields greater than those found in the P spiked cultures. These changes in algal yield, caused by nutrient additions, demonstrate that all of the samples except Site 17 were primarily growth limited by phosphorus and secondarily growth limited by nitrogen.

Site 17, located below Thompson Falls Reservoir, produced erratic results when the N+P spike was added. Test results in the three replicate flasks were 0.49, 19.71 and 5.30 mg dry weight S. capricornutum/liter. These results produced a coefficient of variation of 118% and a mean yield of 8.50 mg dry weight/liter. The addition of N+P+EDTA produced a yield of 39.46 mg dry weight/liter with a coefficient of variation of 9%. This yield is significantly greater than that produced in the N+P spiked flasks and more in line with yields found in all of the other N+P and N+P+EDTA spiked cultures. Erratic results in N+P spiked flasks, coupled with the increased yields in the N+P+EDTA spiked flasks, are indicative of stress caused by inadequate levels of

TABLE II. Mean algal assay yields (mg dry weight/liter) and their associated standard deviation and coefficient of variation for results of tests performed on waters collected from the lower Clark Fork River, MT during December 1984. Assays were performed for 14-days in waters pre-treated by autoclaving followed by filtration.

| SITE No. | CHEM ID (63) | Stats. | Cont-rol | 1.00 mg/l N | 0.05 mg/l P | N+P | 1.00 mg/l EDTA | N+E | P+E | N+P+E | Limiting Nutrient |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10. | 49800 | Mean | 0.10 | 0.07 | 9.90 | 28.73 | 0.09 | 0.10 | 9.75 | 34.64 | p/n |
| | | SD | 0.02 | 0.01 | 0.65 | 9.33 | 0.04 | 0.03 | 0.42 | 2.91 | |
| | | CV | 21 | 20 | 7 | 33 | 47 | 26 | 4 | 8 | |
| 11. | 51801 | Mean | 0.87 | 1.06 | 11.77 | 36.88 | 0.79 | 0.76 | 10.90 | 45.41 | p/n |
| | | SD | 0.12 | 0.11 | 0.52 | 1.78 | 0.06 | 0.03 | 1.32 | 3.09 | |
| | | CV | 14 | 10 | 4 | 5 | 7 | 3 | 12 | 7 | |
| 12. | 51803 | Mean | 1.05 | 0.73 | 12.70 | 43.34 | 1.01 | 0.63 | 12.85 | 44.68 | p/n |
| | | SD | 0.44 | 0.06 | 0.37 | 3.81 | 0.22 | 0.24 | 0.98 | 1.46 | |
| | | CV | 42 | 9 | 3 | 9 | 22 | 38 | 8 | 3 | |
| 13. | 51804 | Mean | 2.41 | 2.30 | 12.97 | 48.74 | 2.95 | 2.98 | 13.59 | 48.35 | p/n |
| | | SD | 0.09 | 0.48 | 1.13 | 3.39 | 0.17 | 0.79 | 0.81 | 1.22 | |
| | | CV | 4 | 21 | 9 | 7 | 6 | 27 | 6 | 3 | |
| 14. | 51802 | Mean | 0.04 | 0.06 | 9.37 | 41.24 | 0.08 | 0.07 | 10.86 | 38.54 | p/n |
| | | SD | 0.12 | 0.02 | 0.63 | 3.59 | 0.03 | 0.02 | 0.51 | 0.32 | |
| | | CV | 30 | 30 | 7 | 9 | 41 | 26 | 5 | < 1 | |
| 15. | 51808 | Mean | 4.73 | 4.56 | 15.61 | 43.33 | 6.18 | 6.44 | 14.92 | 44.78 | p/n |
| | | SD | 2.27 | 1.30 | 0.74 | 2.96 | 0.45 | 0.48 | 1.34 | 2.21 | |
| | | CV | 48 | 28 | 5 | 7 | 7 | 7 | 9 | 5 | |
| 16. | 51807 | Mean | 0.87 | 0.97 | 4.44 | 38.80 | 1.11 | 1.01 | 4.49 | 35.66 | p/n |
| | | SD | 0.10 | 0.15 | 0.36 | 3.09 | 0.14 | 0.21 | 0.16 | 1.75 | |
| | | CV | 12 | 16 | 8 | 8 | 13 | 20 | 4 | 5 | |
| 17. | 51806 | Mean | 0.14 | 0.15 | 7.93 | 8.50 | 0.19 | 0.13 | 5.91 | 39.46 | m/p/n |
| | | SD | 0.05 | 0.08 | 2.96 | 10.00 | 0.11 | 0.01 | 0.19 | 3.48 | |
| | | CV | 40 | 52 | 37 | 118 | 57 | 8 | 3 | 9 | |
| 18. | 51805 | Mean | 2.15 | 2.54 | 8.92 | 39.61 | 2.01 | 1.77 | 8.10 | 39.59 | p/n |
| | | SD | 0.19 | 0.19 | 0.64 | 2.10 | 0.14 | 0.16 | 0.55 | 4.29 | |
| | | CV | 9 | 7 | 7 | 5 | 7 | 9 | 7 | 11 | |

m = Indicates that the sample was growth limited by trace metals (usually un-chelated iron). This conclusion is made when the difference in yields in the control and EDTA spiked flasks is = or > 20%.

CV = The coefficient of variation = standard deviation / mean * 100.

biologically available trace metal nutrients that are essential for growth of S. capricornutum. To prove that trace metals were not immediately available to meet the nutrient requirements of the algae and that heavy metals toxicity was not affecting growth in the Site 17 sample additional test cultures were spiked with phosphorus or nitrogen plus phosphorus and EDTA or trace elements (TE), singly or in combination (Table III).

The 38.17 mg dry weight/liter achieved in cultures spiked with N+P+TE demonstrates that trace elements were the growth limiting constituent. The fact that a similar yield of 39.46 mg dry weight/liter was achieved with the addition of N+P+EDTA indicates that the necessary trace metal nutrients were present in the test water collected from Site 17, but they were not biologically available. Once the trace metal nutrient problem was resolved the Site 17 sample was limited from further growth by phosphorus followed by nitrogen.

With the exception of Site 17, The addition of nutrients in combination with EDTA did not produce algal yields statistically different from those produced in flasks with similar nutrient additions without EDTA. These data indicate that heavy metals did not affect the growth of algae in these test waters either as a growth limiting nutrient or as a toxin.

Although all of the samples were primarily phosphorus and secondarily nitrogen limited their control maximum yields ranged over three orders of magnitude. The lowest control yield (0.04 mg dry weight/liter) was found in the sample collected at Site 14 at Superior, Montana followed by the Site 10 sample collected below Milltown Dam (0.10 mg dry weight/liter). The greatest yield (4.73 mg dry weight/liter) was produced in the sample collected at Site 15 located above the confluence of the Flathead River. The histogram (Figure 1) illustrates the maximum growth potential in controls cultures below Milltown Dam downstream to below Noxon Dam. There is an obvious increase in growth potential (with the exception of Site 14 at Superior) from Site 10 to Site 15. Miller, Maloney and Greene (1974) described a Selenastrum capricornutum productivity subgroup classification system. These subgroups shown on Figure 1 indicate that: Two (22%) of the 9 sites fall within the low productivity subgroup; One (11%) falls within the moderate productivity subgroup; and, Six (67%) fall within the moderately high productivity subgroup.

The orthophosphate concentrations analyzed in these test waters are reported on Table IV. The lack of necessary sensitivity for phosphorus analysis at these low nutrient concentrations did not provide information that would allow definition, with any degree of certainty, of the primary or secondary limiting nutrients. Furthermore, if one studies the total soluble inorganic nitrogen (TSIN) levels presented in Table V one would conclude that a large portion of the nitrogen controlled growth was influenced by organic nitrogen. For example, Site 11 above the Missoula wastewater treatment plant produced a mean control yield of 11.

TABLE III. Growth responses of algae cultured in water collected below Thompson Falls Reservoir and spiked with different combinations of nitrogen, phosphorus, EDTA and trace elements.

****************************************

| SITE No. | CHEM ID (63) | OTHER ADDITIONS | P | N+P |
|---|---|---|---|---|
| 17. | 51806 | None | 7.83 | 8.50 |
| | | EDTA | 5.91 | 39.46 |
| | | TE | 7.17 | 38.17 |
| | | EDTA + TE | 5.98 | 35.19 |

P = 0.05 mg/liter.
N = 1.00 mg/liter.
EDTA= 1.00 mg/liter.
TE = In ug/liter: 32.46 B; 115.37 Mn; 1.57 ZN; 0.35 Co; 2.88 Mo and 33.05 Fe.

FIGURE 1. Productivity classification of lower Clark Fork River

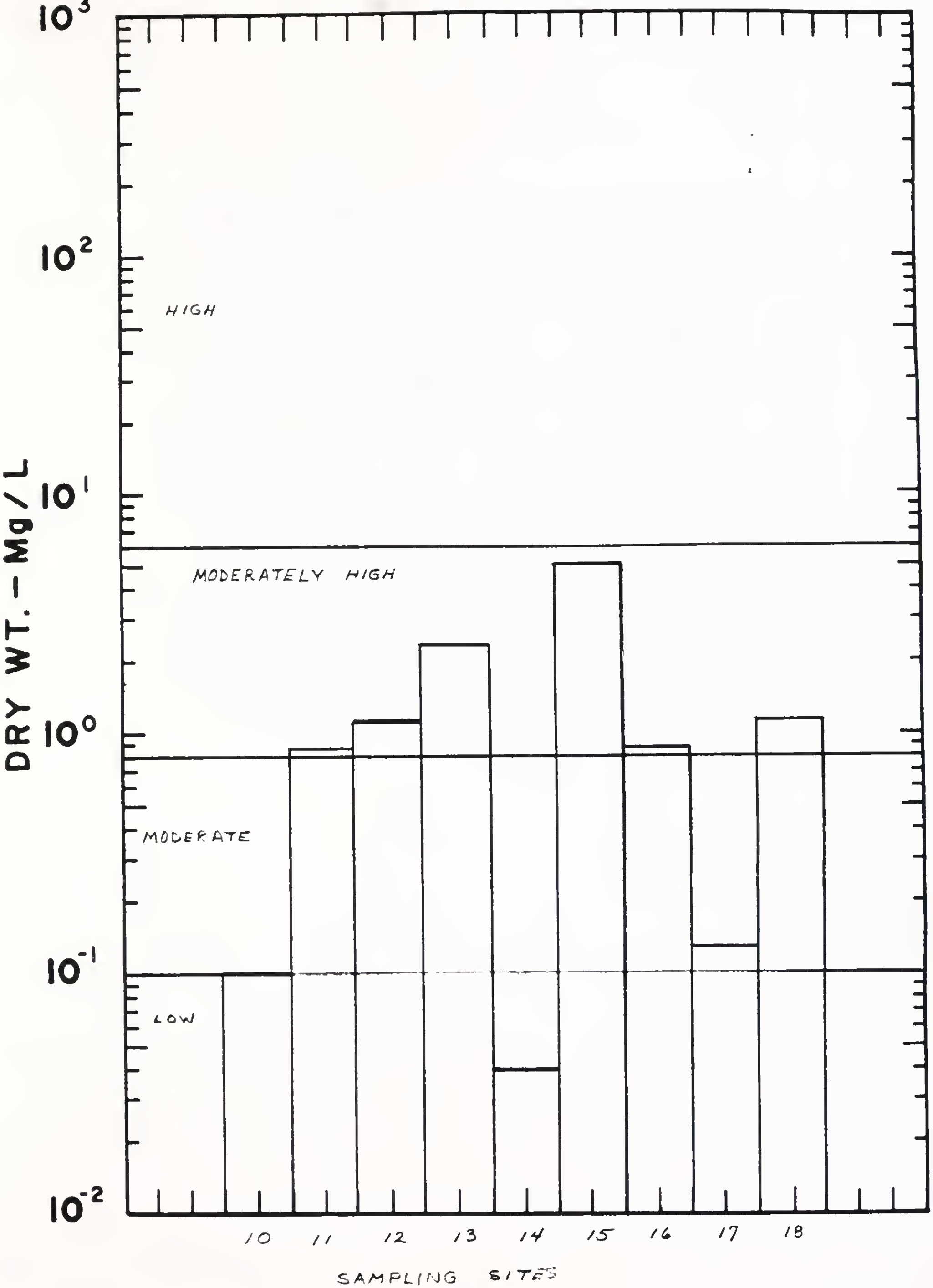

TABLE IV. The relationship between ortho phosphorus defined analytically and by back calculation of phosphorus limited algal growth potential test yields.

| EPA SITE No. | CHEM ID (63) * | P-LIMITED YIELD Mean | SD | **BC Ortho Phos. | Analysed OP CERL | MT |
|---|---|---|---|---|---|---|
| 10. | 49800 | 0.09 | 0.01 | <.001 | <.010 | .010 |
| 11. | 51801 | 0.87 | 0.14 | .002 | <.010 | .010 |
| 12. | 51803 | 0.86 | 0.23 | .002 | <.010 | .010 |
| 13. | 51804 | 2.66 | 0.35 | .006 | <.010 | .020 |
| 14. | 51802 | 0.06 | 0.03 | <.001 | <.010 | .010 |
| 15. | 51808 | 5.48 | 0.71 | .013 | <.010 | .010 |
| 16. | 51807 | 0.99 | 0.10 | .002 | <.010 | <.010 |
| 17. | 51806 | 0.15 | 0.03 | <.001 | <.010 | <.010 |
| 18. | 51805 | 2.12 | 0.03 | .005 | <.010 | <.010 |

* The means of the yields in the Control, N, EDTA and NE spike samples (mg/liter).

** Back calculation is the mean phosphorus limited algal yield divided by 430.

TABLE V. The relationship between analyzed total soluble inorganic nitrogen and total bioavailable nitrogen derived by back calculation of nitrogen limited algal growth potential test yields.

| EPA SITE No. | CHEM ID (63) | N-LIMITED YIELD | | **BC N | ANALYSED TSIN | | ORG. N |
|---|---|---|---|---|---|---|---|
| | | *Mean | SD | | CERL | MT | MT |
| 10. | 49800 | 9.83 | 0.10 | 0.259 | 0.07 | 0.13 | 0.188 |
| 11. | 51801 | 11.34 | 0.58 | 0.298 | 0.11 | 0.13 | 0.192 |
| 12. | 51803 | 12.78 | 0.12 | 0.336 | 0.18 | 0.14 | 0.251 |
| 13. | 51804 | 13.28 | 0.46 | 0.349 | 0.14 | 0.15 | 0.282 |
| 14. | 51802 | 10.12 | 1.05 | 0.266 | 0.09 | 0.09 | 0.181 |
| 15. | 51808 | 15.27 | 0.61 | 0.402 | 0.14 | 0.07 | 0.109 |
| 16. | 51807 | 4.47 | 0.04 | 0.118 | 0.01 | 0.03 | 0.201 |
| 17. | 51806 | 6.92 | 0.90 | 0.182 | 0.01 | 0.02 | 0.101 |
| 18. | 51805 | 8.51 | 0.58 | 0.224 | 0.02 | 0.03 | 0.203 |

* The means of the yields in the nitrogen and nitrogen + EDTA spiked samples (mg/liter).

** Back calculation is the mean nitrogen limited algal yield divided by 38.

mg dry weight/liter. The yield divided by 38 (Shiroyama, Miller and Greene, 1973; Greene et al., 1975) indicated that 0.310 mg total nitrogen/liter was required to achieve this quantity of algal biomass. The ISIN analyzed at CERL was 0.110 mg/liter. This concentration of ISIN is only 36% of the nitrogen required to produce the 11.77 mg dry weight/liter. CERL did not analyze for organic nitrogen but, the State of Montana did. Their 0.192 mg organic nitrogen/liter added to the 0.110 mg ISIN/liter analyzed at CERL amount to 0.302 mg total nitrogen/liter or 103% of the amount required to produce 11.77 mg dry weight S. capricornutum/liter. This type of biological test result demonstrates why one must exercise caution when chemically derived inorganic N:P ratios are used for predicting algal growth limiting nutrients.

## REFERENCES

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# RESULTS OF ALGAL ASSAYS PERFORMED ON WATERS COLLECTED FROM THE LOWER CLARK FORK RIVER SYSTEM AT STATIONS BELOW MILLTOWN DAM TO BELOW NOXON DAM

## Report II: May 10-16, 1985 Sampling

by
Joseph C. Greene, Michael Long, Cathy Lee Bartels
and Julius U. Nwosu

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## INTRODUCTION

A large amount of public concern has been expressed over the general health of the lower Clark Fork River system. The proposed modification of the existing wastewater discharge permit for the Champion International paper mill at Frenchtown has generated much of this concern. Other sources of wastewater, namely the City of Missoula wastewater treatment plant and historic metals deposits originating upstream from Milltown Dam, have also been mentioned as possible sources of stress on the river (Montana, 1984).

The Selenastrum capricornutum algal assays performed during this study were undertaken to fulfill a request for technical assistance from the Montana Water Quality Bureau through the US EPA Region VIII staff in Denver, CO. The Montana Department of Health and Environmental Services has a Lower Clark Fork River Monitoring Plan. Data gathered from these assays will be used in conjunction with other date collected under this monitoring plan to define existing conditions in the Lower Clark Fork River system.

## METHODS

Water was collected, as surface grab samples, along the Clark Fork River (Table 1) by Montana Department of Health and Environmental Sciences and US Environmental Protection Agency Region VIII scientists. River water collected at each site was transported to an EPA mobile field laboratory located at Frenchtown, MT. Upon arrival each sample was well mixed and 1125 mls was dispensed into the appropriated, labeled 8000 ml autoclavable polypropylene shipping bottle. Each day from May 10 to 16, inclusive, 1125 mls of the river water was added to the appropriate polypropylene

TABLE I.

## CLARK FORK RIVER

## SITE IDENTIFICATION

| MT | EPA | |
|---|---|---|
| 4 | 10 | Below Milltown Dam |
| 6 | 11 | Above Missoula WWTP |
| 11 | 12 | At Harper Bridge (above Champion) |
| 15 | 13 | At Huson (below Champion) |
| 20 | 14 | At Superior |
| 22 | 15 | Above Flathead River confluence |
| 25 | 16 | Above Thompson Falls Reservoir |
| 27 | 17 | Below Thompson Falls Reservoir |
| 29 | 18 | Below Noxon Dam |

bottle until a 7-day composite of 7825 mls was achieved. Cooling of the samples during storage was provided by pumping river water continuously into a 1000 gallon tank. Bottles were floated in this tank which maintained the temperature at 12.5 to 13.5 °C. The tank was covered to keep the samples in the dark to inhibit photosynthesis. On May 16, the last day of sampling, at 3:30 pm the samples were delivered to the US Postal Service at Missoula, MT, for delivery to the US EPA Corvallis Environmental Research Laboratory, OR, (CERL) for testing by the *Selenastrum capricornutum* Algal Assay Bottle Test (Miller, Greene and Shiroyama, 1978). The samples arrived at Corvallis, 8 days later, on the morning of the 24th. They were stored in the dark at 4 °C. Processing, by autoclaving followed by filtration (AF), occurred on May 28, 29 and 30. The samples were autoclaved in their polypropylene shipping bottles. Prior to filtration they were cooled to room temperature and re-equilibrated to their original pH.

The assays, performed with three replicate flasks for each nutrient or chelator addition, were inoculated with a final concentration of 1000 cells *S. capricornutum*/ml and cultured for 14 days. Yields were reported as milligrams dry weight/Liter.

All applicable QA/QC procedures outlined in the HAAL quality assurance plan (US EPA, 1984) were strictly adhered to.

Elemental chemical analysis was performed on an inductively coupled plasma atomic emission spectrometric instrument (ICPAES) according to the USEPA (1983) method for trace element analysis of water and wastes.

## RESULTS AND DISCUSSION

The preferred method of test water pretreatment for algal growth potential testing is autoclaving followed by filtration. The AF pretreatment lyses filterable organisms and returns much of the nutrients contained within them back into solution. A water sample which has been pretreated only by filtration can seriously under estimate the productivity potential of a test water, if a large amount of phytoplankton is present, because nutrients for growth potential are left on the filter. This report discusses the results of algal assay performed on waters pretreated by autoclaving followed by filtration.

The 14-day mean maximum growth potential results for each set of test flasks with their associated standard deviation and coefficient of variation are shown in Table II. Only Site #10 below Milltown Dam was growth limited primarily by phosphorus and secondarily by nitrogen. The following six downstream stations (Sites #11 to #16) were reversed in their nutrient limitation. They were limited from further growth primarily by nitrogen and secondarily by phosphorus. Yields in Site #17 and #18 samples were too close to distinguish which nutrient was primarily

TABLE II.
Algal growth potential results from 14-day tests performed on autoclaved and filtered (AF) waters collected from the lower Clark Fork River during May 1985.

| SITE No. | CHEM. ID (63) | Stats. | Control | 1.00 mg/l N | 0.05 mg/l P | N+P | 1.00 mg/l EDTA | N+E | P+E | N+P+E | Limit. Nutr. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10. | 20838 | Mean | 1.07 | 1.16 | 2.96 | 34.60 | 0.65 | 0.92 | 2.81 | 39.62 | p/n |
| | | SD | 0.43 | 0.12 | 0.87 | 1.59 | 0.12 | 0.05 | 0.18 | 4.27 | |
| | | CV (%) | 41 | 10 | 29 | 5 | 14 | 6 | 7 | 11 | |
| 11. | 20841 | Mean | 3.67 | 9.75 | 3.82 | 37.96 | 4.51 | 10.94 | 4.33 | 45.17 | n/p |
| | | SD | 0.17 | 1.53 | 0.19 | 2.71 | 0.49 | 1.95 | 0.18 | 1.70 | |
| | | CV (%) | 5 | 16 | 5 | 7 | 11 | 18 | 4 | 4 | |
| 12. | 20844 | Mean | 3.05 | 5.73 | 1.83 | 29.69 | 2.95 | 4.78 | 2.47 | 33.58 | n/p |
| | | SD | 0.52 | 1.33 | 0.12 | 5.17 | 0.51 | 0.52 | 0.30 | 4.17 | |
| | | CV (%) | 17 | 23 | 6 | 17 | 17 | 11 | 12 | 12 | |
| 13. | 20847 | Mean | 4.95 | 17.68 | 4.73 | 39.84 | 5.23 | 21.46 | 5.27 | 45.94 | n/p |
| | | SD | 0.55 | 1.95 | 0.16 | 1.66 | 0.45 | 0.78 | 0.27 | 3.04 | |
| | | CV (%) | 11 | 11 | 3 | 4 | 9 | 4 | 5 | 7 | |
| 14. | 20850 | Mean | 4.77 | 14.60 | 5.97 | 38.06 | 5.92 | 19.01 | 6.11 | 45.96 | n/p |
| | | SD | 0.82 | 4.28 | 0.13 | 4.29 | 0.35 | 1.09 | 0.30 | 2.13 | |
| | | CV (%) | 17 | 29 | 2 | 11 | 6 | 6 | 5 | 5 | |
| 15. | 20853 | Mean | 1.97 | 5.62 | 3.83 | 30.43 | 3.54 | 6.25 | 4.01 | 38.83 | n/p |
| | | SD | 0.16 | 4.08 | 0.53 | 1.65 | 0.23 | 1.10 | 0.28 | 2.25 | |
| | | CV (%) | 9 | 73 | 14 | 5 | 7 | 18 | 7 | 6 | |
| 16. | 20856 | Mean | 4.06 | 7.15 | 4.47 | 40.46 | 4.72 | 9.29 | 4.30 | 41.89 | n/p |
| | | SD | 0.18 | 3.62 | 0.41 | 2.97 | 0.49 | 1.20 | 0.11 | 3.15 | |
| | | CV (%) | 4 | 51 | 9 | 7 | 11 | 13 | 3 | 8 | |
| 17. | 20859 | Mean | 2.03 | 3.46 | 2.90 | 32.12 | 3.19 | 2.81 | 3.41 | 36.75 | n+p |
| | | SD | 0.61 | 0.42 | 0.45 | 3.07 | 0.26 | 0.50 | 0.06 | 3.69 | |
| | | CV (%) | 29 | 12 | 15 | 10 | 8 | 18 | 2 | 10 | |
| 18. | 20862 | Mean | 1.71 | 1.02 | 1.62 | 24.83 | 1.23 | 2.51 | 1.84 | 27.55 | m/p+n |
| | | SD | 0.65 | 0.59 | 0.39 | 8.02 | 0.53 | 0.49 | 0.21 | 5.85 | |
| | | CV (%) | 38 | 58 | 24 | 32 | 57 | 20 | 11 | 21 | |

m = Indicates that the sample was growth limited by trace metals. This conclusion is made when the yield in EDTA spiked flasks is = or > 20% of the growth in similar flasks without EDTA.

Cv= The standard deviation divided by the mean times 100.

limiting growth. The two stations have, therefore, been classed as co-limited from further growth by both nitrogen and phosphorus.

According to the productivity classification of Miller, Maloney and Greene (1974) all of the control and EDTA spiked flask yields (Figure 1), regardless of the primary limiting nutrient, fell within the moderately high productivity subgroup (0.81-6.00 mg dry weight/Liter). It can be clearly seen on Figure 1 that the general trend was an increase in productivity from below Milltown Dam (Site #10) to Superior (Site #14) followed by decreasing productivity at Sites #15 to #18. The algal growth potential below Noxon Dam (Site #18) was 121% of the maximum yield achieved in the most upstream station (Site #10 below Milltown Dam) tested during this study.

Analysis of the metals present in these autoclaved and filtered test waters are shown in Table III. All of the potentially toxic heavy metals originating from the upstream Silver Bow Creek sites are below detection. These analytical results are supported by the bioassay test results in that no inhibition of algal growth was demonstrated.

Results of chemical analysis for ortho phosphorus and total phosphorus are shown, along with their algal growth back calculated phosphorus concentrations, in Table IV. Algal growth back calculated phosphorus concentrations were obtained by dividing the mean maximum phosphorus limited algal yields by 430. These calculations establish the mg phosphorus/Liter required to produce the yields achieved in these test cultures. The theory behind this approach is that S. *capricornutum* will produce .430 mg dry weight/Liter for each .001 mg phosphorus/Liter that is biologically available in the water sample (Shiroyama, Miller and Greene, 1975).

It is generally accepted that ortho phosphorus is the species most readily available for algal nutrition. If this is true, and the biological and analytical systems are operating efficiently, the algal growth back calculated results should mirror the analyzed ortho phosphorus results. In fact, this is the case for samples collected at Sites #12, 15, 17 and, perhaps, Site #18. However, calculation of algal growth results from Sites #11, 14 and 16 more closely reflect the samples total soluble phosphorus content. The analysis of phosphorus in the Site #13 sample is anomalous in that the amount of nutrients required to achieve the algal yield (0.046 mg P/Liter) was almost double the concentration reported for ortho or total phosphorus. These data point out the danger of predicting algal growth potential from the results of chemical analysis for phosphorus only. Often the environmental concentrations of phosphorus are at or near the usual lower sensitivity limits (0.010 mg P/Liter) of chemical analysis for this element. This fact, coupled with the knowledge that phosphorus limited samples containing from 0.002 to 0.016 mg P/Liter produce enough algal growth to fall within the moderately high productivity classification should warn one to exercise

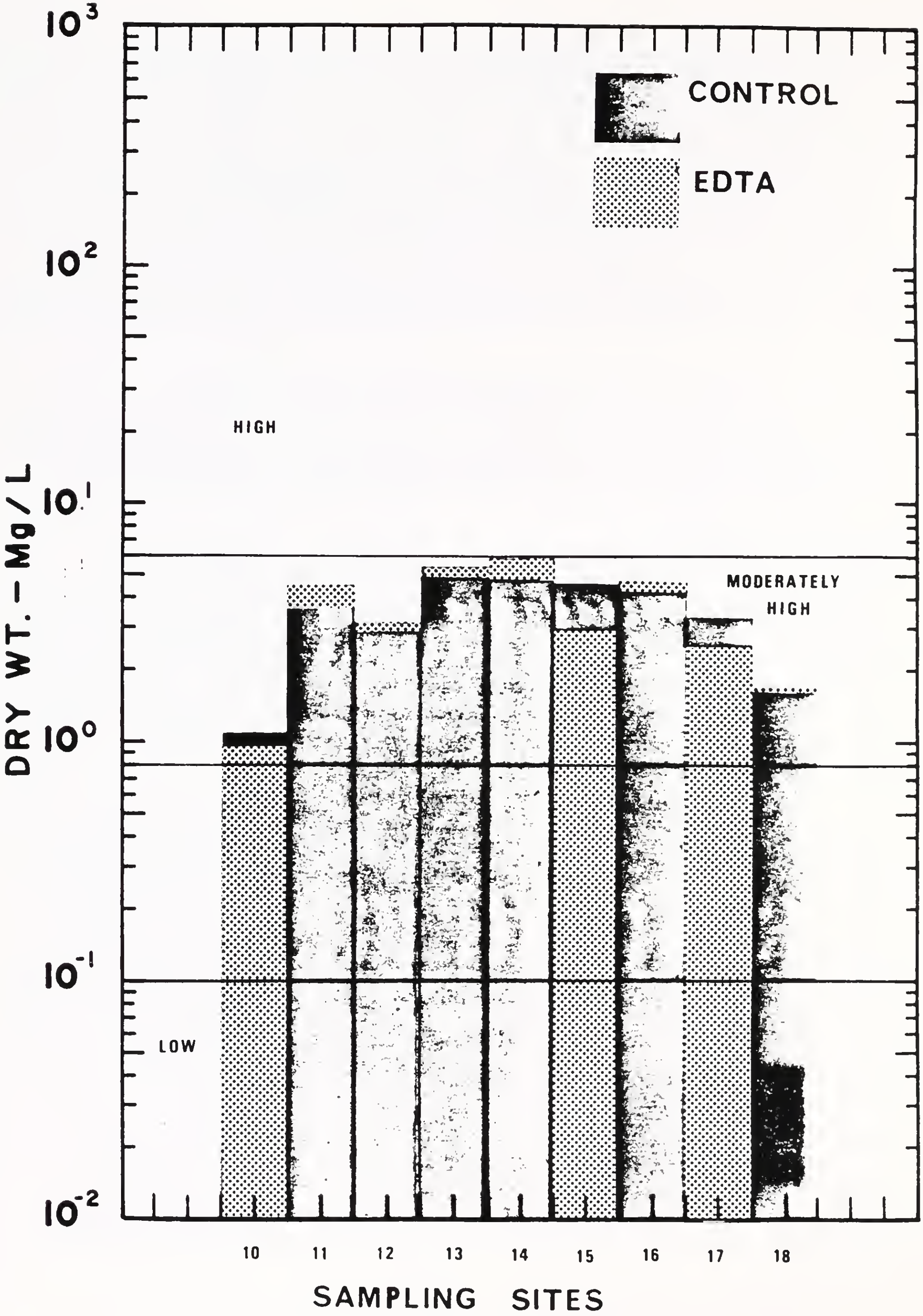CONTROL
EDTA
HIGH
MODERATELY HIGH
LOW
$10^3$
$10^2$
$10^1$
$10^0$
$10^{-1}$
$10^{-2}$
DRY WT. – Mg/L
10
11
12
13
14
15
16
17
18
SAMPLING SITES

TABLE III.
Analytical results of metal concentrations found in waters collected from the lower Clark Fork River system during May 1985.

| SITE No. | Chem. ID (6320) | milligrams / liter |  |  |  |  |  |  |  |  |  |  |  | * Calc. Hardness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Zn | Cu | Cd | Ni | Ca | Mg | Cr | As | Pb | Al | Mn | S |  |
| 10 | 838 | <.002 | <.002 | <.003 | <.006 | 14.85 | 4.24 | <.004 | <.015 | <.025 | <.025 | <.001 | 5.37 | 55 |
| 11 | 841 | <.005 | <.003 | <.005 | <.006 | 22.03 | 6.38 | <.004 | <.015 | <.025 | <.025 | .003 | 4.25 | 81 |
| 12 | 844 | <.002 | <.002 | <.005 | <.006 | 16.57 | 2.38 | <.004 | <.015 | <.025 | <.025 | <.001 | 3.55 | 51 |
| 13 | 847 | <.003 | <.003 | <.005 | <.006 | 14.54 | 4.60 | <.004 | <.015 | <.025 | <.035 | .003 | 3.62 | 55 |
| 14 | 850 | <.005 | <.003 | <.005 | <.006 | 17.75 | 4.72 | <.004 | <.015 | <.025 | <.051 | .003 | 3.41 | 64 |
| 15 | 853 | <.003 | <.002 | <.004 | <.008 | 11.11 | 3.71 | <.004 | <.015 | <.025 | <.025 | <.001 | 3.34 | 43 |
| 16 | 856 | <.003 | <.002 | <.003 | <.006 | 21.97 | 5.53 | <.004 | <.015 | <.025 | <.027 | .003 | 3.22 | 78 |
| 17 | 859 | <.003 | <.002 | <.004 | .012 | 20.41 | 3.94 | <.004 | <.015 | <.030 | <.025 | <.001 | 2.43 | 67 |
| 18 | 862 | <.003 | <.002 | <.005 | <.007 | 19.05 | 4.73 | <.004 | <.015 | <.025 | <.027 | <.001 | 2.47 | 67 |

* Hardness was calculated using Standard Method 314A (APHA, 1985).

TABLE IV.
The relationship between analyzed ortho phosphorus and results derived from back calculation of phosphorus limited algal growth potential test results.

| EPA SITE No. | CHEM ID (63) | P-LIMITED YIELD | | **BC Ortho Phos. | Analyzed P | |
|---|---|---|---|---|---|---|
| | | * Mean | SD | | Ortho | Total |
| 10. | 20838 | 1.01 | 0.15 | 0.002 | .006 | .019 |
| 11. | 20841 | 10.35 | 0.84 | 0.024 | .012 | .024 |
| 12. | 20844 | 5.26 | 0.67 | 0.012 | .013 | .042 |
| 13. | 20847 | 19.57 | 2.67 | 0.046 | .022 | .024 |
| 14. | 20850 | 16.81 | 3.12 | 0.039 | .020 | .039 |
| 15. | 20853 | 5.84 | 0.30 | 0.014 | .021 | .033 |
| 16. | 20856 | 8.22 | 1.51 | 0.019 | .011 | .021 |
| 17. | 20859 | 3.14 | 0.46 | 0.007 | .008 | .038 |
| 18. | 20862 | 1.57 | 0.71 | 0.004 | <.005 | .035 |

* The mean of yields in the phosphorus limited samples (mg dry weight/liter).

** Back calculation is the mean phosphorus limited algal yield divided by 430.

caution when making algal productivity predictions on phosphorus analysis alone.

Results of chemical analysis for total soluble inorganic nitrogen (TSIN = $NO_2 + NO_3 + NH_3$) and organic nitrogen are shown in Table V along with their associated alga growth calculated bioavailable nitrogen concentrations. Algal growth back calculated nitrogen concentrations were obtained by dividing the mean maximum nitrogen limited algal yields by the coefficient 38. These calculations resulted in an estimate of the amount of bioavailable nitrogen in each sample. According to Shiroyama, Miller and Greene (1975) S. capricornutum will produce .038 mg dry weight/Liter for each .001 mg/Liter nitrogen that is biologically available.

It is generally assumed that TSIN is biologically available for utilization by algae. However, in addition to TSIN, certain species of organic nitrogen are also utilized in the production of algal biomass. All of the nine samples in this study have produced some biomass from organic nitrogen. Organic nitrogen produced from 11% (Site #15) to 81% (Site #11) of the algal growth potential in these studies. It can be clearly seen in Table V that the amount of nitrogen required to produce the nitrogen limited algal yield (back calculated) is, in every case, greater than the analyzed TSIN. If the inorganic nitrogen analysis is correct, which we assume it is, then the growth above that level that could be produced by the TSIN must come from organic nitrogen.

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Shiroyama, T., W.E. Miller and J.C. Greene. 1975. Effect of

TABLE V.
The relationship between analyzed total soluble inorganic nitrogen and total bio-available nitrogen derived from back calculation of nitrogen limited algal growth potential test results.

| EPA SITE No. | CHEM ID (63) | N-LIMITED YIELD *Mean | SD | **BC N | ANALYSED TSIN | ORG-N |
|---|---|---|---|---|---|---|
| 10. | 20838 | 2.89 | 0.11 | 0.076 | <.010 | 0.162 |
| 11. | 20841 | 4.08 | 0.40 | 0.107 | <.010 | 0.133 |
| 12. | 20844 | 2.58 | 0.56 | 0.068 | .033 | 0.113 |
| 13. | 20847 | 5.05 | 0.25 | 0.133 | .031 | 0.176 |
| 14. | 20850 | 5.69 | 0.62 | 0.150 | .052 | 0.338 |
| 15. | 20853 | 3.33 | 0.93 | 0.088 | .057 | 0.284 |
| 16. | 20856 | 4.39 | 0.27 | 0.116 | .013 | 0.160 |
| 17. | 20859 | 2.90 | 0.58 | 0.076 | .021 | 0.215 |
| 18. | 20862 | 2.23 | 0.86 | 0.059 | <.010 | 0.273 |

* The means of the yields in the nitrogen and nitrogen plus EDTA spiked samples (mg dry weight/liter).

** Back calculation is the mean nitrogen limited algal yield divided by 38.

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## C. CHRONIC TOXICITY BIOASSAYS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION VIII
ONE DENVER PLACE — 999 18TH STREET — SUITE 1300
DENVER, COLORADO 80202-2413

AUG 0 6 1985

Ref: 8WM-SP

MEMORANDUM

TO: Steve Pilcher, WQB
Montana Department of Health
and Environmental Services (DHES)

FROM: Del Nimmo, 8WM-SP DN
U.S. Environmental Protection Agency,
Region VIII

SUBJECT: Preliminary Findings of Chronic Bioassays at Champion International Pulp Mill/Lower Clark Fork River Site.

Attached is an interim report of the findings of a chronic bioassay conducted from May 31, 1985 to June 12, 1985 at the Champion International site. You should be aware that final tabulation of data is incomplete, i.e. neither standard deviations and ranges are presented nor have all data been analyzed for statisticial significance using more than one method. All data, results and conclusions must be considered provisional at this time although inferences drawn from the data on test organisms can be used for purposes of planning additional studies. A more thorough and complete report will be available in a few weeks.

Summary: Report on the Preliminary Findings of Chronic Bioassays at Champion International Pulp Mill/Lower Clark River Fork River Site.

## INTRODUCTION

Personnel from EPA's Region VIII, National Enforcement Investigations Center (Denver), EPA's Montana Operations Office (Helena) and Montana's Department of Health and Environmental Sciences (Helena), conducted chronic bioassays using rainbow trout (button-up stage) and *Ceriodaphnia* at the Champion International/Clark Fork River site. Dates for the study were scheduled from May 4 through June 3, 1985 but because of delays, actual dates for testing were May 13 to June 12, 1985. The delay was due primarily to the lack of a sufficient number of fish at the proper life-stage (button-up) at the time scheduled for beginning the study. Approximately 10 days were spent waiting for the fish to mature to the appropriate stage of active feeding as called for in the test procedures (Attachment A). During this time of acclimation and maturing of the fish, a chronic test was conducted with *Ceriodaphnia* using Champion's wastewater with two dilution waters, Clark Fork River water and well water. In addition, during the 30-day test with the trout, a 7-day *Ceriodaphnia* chronic test was conducted using daily instream grab samples of Clark Fork on eight stations beginning from below Milltown Dam and continuing downstream to below Noxon Dam. This study provided a profile of potential toxicity of the Clark Fork river water.

## ALTERATIONS OF TEST PROCEDURES AND CONDITIONS

Several alterations were made in the test procedure. The most important change was the use of a different range of test dilutions than those proposed in the test procedures. Instead of waste dilutions ranging from 1/10 to 1/1000 as stated in the test procedures, a more restrictive series was used but with the same median dilutions as originally outlined. The reason for this change was the physical sizes of the diluter-cell volumes (permanently constructed). Therefore, the series of Champion wastewater to river water dilutions were 4/200; 3/200; 2.24/200; 1.28/200; 0.72/200; 0.4/200, and 0/200. Likewise, the other dilution series, conducted concurrently with Champion wastewater to Champion unchlorinated well water was 4/200; 3/200; 2.24/200; 1.28/200; 0.72/200; 0.4/200, and 0/200. The result of both series was a median dilution of 1/200 between 1.28/200 and 0.72/200 diluter setting. In terms of percentages of wastewater to dilution water, the series was 2, 1.5, 1.12, 0.64, 0.36, 0.2, and 0 (control) percent. Eighty fish were used in each test dilution.

One unfortunate event interrupted an otherwise problem-free study at Champion. On day 12, a drain system evacuating test water from each of the test aquaria, became clogged. As a result, volumes of test dilutions delivered to aquaria, were not drained. The aquaria finally filled and overflowed into the temperature control bath. As this process was occurring, test fish escaped into the bath, and finally mixed with fish in other aquaria. Consequently, some aquaria (and data) could not be used in the analyses, and others had reduced numbers of fish per aquaria. These aquaria are identified in the following tables.

# RESULTS AND DISCUSSIONS

## MORTALITY OF FISH

Mortality during the tests was extremely low in both river water and well water dilutions. Using a base of 80 fish per dilution, the percentage of deaths were 10% or less in the dilutions of river water; 8.75% or less in the well water dilutions. No fish died in the last nine days in the well water and only one died in the last ten days in the river water dilutions. Approximately half of the fish that died in the first 20 days of the test were recorded as "pinheads" or non-feeding larvae.

## GROWTH OF FISH

Means of condition coefficients, determined by dividing the wet weight by the $(\text{length})^3$, are shown in Table 1. Although significant differences occurred between several groups and controls (0.0) there was no clear dose response relationship with wastewater dilution. In a couple of dilutions, due to more fish in the aquaria as a result of the upset and co-mingling, the data were tabulated but should not be considered in the analysis. We note that in most cases, the fish were larger in the groups exposed in river water dilutions than in the well water dilutions.

## CERIODAPHNIA GROWTH AND REPRODUCTION IN WASTEWATER

Tests with Ceriodaphnia (chronic seven-day static renewal) using wastewater and dilutions of well water were not considered acceptable for analysis. Mortality of control daphnids, as well as all other dilutions was greater than 20%. Control mortality was 60% in this study, indicating something in the test dilution (well) water was incompatible to the survival of daphnids.

Tests with the daphnids and wastewater diluted with river water were completed successfully and these data are shown in Table 2. Using the 95% confidence intervals to indicate significant differences, the number of neonates produced per female was lower in the 4% (8/200) dilution than in control. We also noted that reproductive success of the 4% dilution-group of daphnids was less than in the 0.2, 0.36, 1.12, 1.5, dilutions as well.

## CERIODAPHNIA GROWTH AND REPRODUCTION, ABOVE AND BELOW CHAMPION'S OUTFALL

Using ambient water from river stations above and below Champion's outfall as test dilutions, Ceriodaphnia survived and reproduced in water at all locations (Table 3). Survival exceeded 90% in all cases and reproduction in water from all stations exceeded the controls in the previous tests (Table 2). In these tests stations 10, 11, and 12 were considered as "controls" because they were upstream of Champion's outfall. Stations 14 through 18 are considered as "treatment or test" stations because they are below Champion. Interestingly, there were no statistical differences among any stations with respect to survival (all greater than 90%), or reproduction (Table 3), except that station 13 (Huson below Champion), reproduction (measured as number of young per female) was significantly greater than all others. This difference was significant even though 3, 4, or 5 brood release were considered in the calculation. For example, almost 40 neonates per female were produced on day 7; whereas between 30 to 34 were produced, on the average, at the other eight stations.

## ANALYSES OF CHEMICAL CONSTITUENTS

Summaries of chemical constituents measured during the testing are shown in Attachments B and C. Inspection of these data indicate characteristics of test dilutions were similar among dilutions of well water and river water. Total ammonia and temperatures were virtually identical. The pH was higher in well water dilutions along with conductivity, calcium, magnesium, and alkalinity. Concentrations of dissolved sulfide was greater in dilutions of river water than well water as were concentrations of dissolved organic carbon and total organic carbon. Concentrations of dissolved oxygen throughout the test aquaria were essentially identical and above acceptable limits for trout, although we noted that the decision to deliver compressed air to test aquaria was due to lowered dissolved oxygen in dilutions of well water vs. the river water.

Analysis of 100 percent Champion wastewater, Champion's well water, and the Clark Fork River above Champion's outfall on two different sampling dates did not reveal concentrations of toxic materials (priority pollutants) (Attachments D and E). Of note were concentrations of natural acids, ketones and alcohols in Champion's wastewater with most of these substances higher in the 5/17/85 sample that the 5/31/85 sample.

Analyses of metals by ICAP on two sampling dates did not show any metals at concentrations believed to be toxic. Of interest was the concentration of aluminum in Champion's wastewater of 4860 ug/l in the 5/17/85 sample and 3440 ug/l in the 5/31/85 sample. Freeman and Everhart [1971, Trans. Am. Fish. Soc. 100 (4): 544-658] found that aluminum salts were slightly soluable at pH of about 7.0 and had little effect in rainbow trout. As the pH was raised, greater amounts of aluminum became dissolved and therefore, more toxic. Likewise, studies of acid precipitation suggest that at lower pH, e.g. 5-6, aluminum is also mobilized and more toxic. Important to consider in the tests at Champion was that the maximum concentrations of aluminum in the test aquaria were only two percent of those concentrations shown in the analyses because of the dilution factors.

# CONCLUSIONS AND SUGGESTIONS

There are no data in this study that suggest the current permit limits nor conditions should be changed for Champion International. We suggest that perhaps additional studies should be conducted using only Clark Fork River as dilution water and thus making two dilutions available and allowing a greater number of test fish per dilution. Perhaps an eight-day-growth study with post button-up stage rainbow trout, tested in two identical diluter systems, with at least 160 fish per dilution would provide sufficient numbers to detect subtle effects on growth. In addition, at least two *Ceriodaphnia* tests should be conducted in concert with a benthic species of insect or crustacean to address potential effects of the wastewater on benthic communities downstream. A sampling station closer to the Champion's outfall (i.e. 1 mile) should also be considered instead of the one used in this study, and that future tests include a test of the "seepage effluent" entering the river from the lagoons.

## Table 1

Means ($\bar{x}$) and 95% Confidence Intervals of Condition Coefficients of Rainbow Trout, Tested in Various Dilutions of Champion International Wastewater.

RIVER WATER

| Percentage Wastewater Dilution | Means (x) Condition Coefficient | 95% Confidence Interval | Number of Fish Per Dilution |
|---|---|---|---|
| 0.0 | 173.7 | 166.9-180.5 | 56 |
| 0.2 | 182.7 | 176.8-188.7[3] | 85 |
| 0.36 | 164.4 | 156.7-172.2 | 66 |
| 0.64 | 160.0 | 152.5-167.4 | 58 |
| 1.12 | 159.0 | 154.4-163.6[2] | 76 |
| 1.5 | 148.3 | 142.6-154.1[2] | 48 |
| 2.0 | 173.2 | 168.8-177.6 | 33 |

WELL WATER

| | | | |
|---|---|---|---|
| 0.0 | 164.0 | 158.2-169.7 | 49 |
| 0.2 | 146.9 | 143.7-150.0[3] | 111 |
| 0.36 | 172.2 | 166.9-177.6 | 70 |
| 0.64 | 175.9 | 171.9-179.9[2] | 74 |
| 1.12 | 175.0 | 168.5-181.5 | 33 |
| 1.5 | 159.3 | 150.3-168.3[2] | 39 |
| 2.0 | 167.6 | 162.8-172.3 | 49 |

[1] Condition Coefficient was calculated by dividing the wet weights of each fish (alive) at the end of the study by the $(\text{length})^3$, multiplied times $10^4$. This procedure provides a measure of the "health or plumpness" of the fish expressed as whole numbers.

[2] Significantly different from control fish based on 95% confidence limits.

[3] Excluded from analysis due to co-mingling of fish.

Table 2

Means ($\bar{x}$), Standard Deviations (S.D.) and Confluence Intervals of *Ceriodaphnia* Reproduction, Tested in Various Dilutions of Champion International Wastewater Diluted with River Water

| Percentage Wastewater Dilution | Number of Living Daphnids | Mean Number of Neonates Prod. | Standard Deviation (S.D.) | 95% Confidence Interval |
|---|---|---|---|---|
| 0.0 | 8 | 10.6 | 4.93 | 6.5-14.7 |
| 0.2 | 9 | 9.9 | 3.48 | 7.2-12.6 |
| 0.36 | 9 | 10.9 | 6.64 | 5.8-16.0 |
| 0.64 | 9 | 6.6 | 3.17 | 4.2- 9.0 |
| 1.12 | 9 | 12.2 | 6.44 | 7.2-17.2 |
| 1.5 | 10 | 10.1 | 4.86 | 6.6-13.6 |
| 2.0 | 10 | 9.9 | 6.92 | 4.9-14.9 |
| 4.0 | 9 | 3.4[1] | 3.13 | 1.0- 5.8 |

[1] Significantly different from controls (0.0) at $P \leq 0.05$.

Table 3

Average Number ($\bar{x}$) of Neonates Produced Per Female *Ceriodaphnia* in Seven Consecutive Daily Samples of Clark Fork River Water Taken From Nine Stations.

| Station | Description | Mean | 95% Confidence Interval |
|---|---|---|---|
| | - Data from Total of Five Broods - | | |
| 10 | CFR Below Milltown Dam | 30.6 | 26.2-35.0 |
| 11 | CFR Above Missolua WWTP | 30.0 | 28.4-31.6 |
| 12 | CFR Harper Bridge | 30.6 | 27.8-33.4 |
| 13 | CFR At Huson (below Champion) | 39.9 | 35.9-43.9[1] |
| 14 | CFR At Superior | 32.1 | 30.3-33.9 |
| 15 | CFR Above Flathead confl. | 33.8 | 28.9-38.7 |
| 16 | CFR Thompson Falls | 30.2 | 27.5-32.9 |
| 17 | CFR Below Thompson Falls | 30.6 | 28.1-33.1 |
| 18 | CFR Below Noxon Dam | 31.3 | 28.7-33.9 |
| | -Data from Total of Four Broods - | | |
| 10 | CFR Below Milltown Dam | 29.6 | 26.3-32.9 |
| 11 | CFR Above Missoula WWTP | 30.0 | 28.4-31.6 |
| 12 | CFR Harper Bridge | 29.3 | 27.3-31.3 |
| 13 | CFR At Huson (Below Champion) | 35.4 | 33.7-37.1[1] |
| 14 | CFR At Superior | 32.1 | 30.3-33.9 |
| 15 | CFR Above Flathead Confl. | 30.0 | 28.0-32.0 |
| 16 | CFR Above Thompson Falls | 29.1 | 27.5-30.7 |
| 17 | CFR Below Thompson Falls | 29.1 | 27.6-30.6 |
| 18 | CFR Below Noxon Dam | 31.3 | 28.7-33.9 |
| | -Data from Total of Three Broods - | | |
| 10 | CFR Below Milltown Dam | 21.0 | 19.4-22.6 |
| 11 | CFR Above Missoula WWTP | 20.0 | 18.9-21.1 |
| 12 | CFR Harper Bridge | 19.8 | 18.5-21.1 |
| 13 | CFR At Huson (below Champion) | 23.4 | 22.5-24.3[1] |
| 14 | CFR At Superior | 21.3 | 20.3-22.3 |
| 15 | CFR Above Flathead confl. | 19.9 | 18.9-20.9 |
| 16 | CFR Above Thompson Falls | 19.9 | 18.9-20.9 |
| 17 | CFR Below Thompson Falls | 19.4 | 17.9-20.9 |
| 18 | CFR Below Noxon Dam | 21.3 | 19.3-23.3 |

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[1] Significantly different from other stations, i.e. greater number of neonates produced per female.

ATTACHMENT A

# Outline for Chronic Fish Bioassay: Champion International Paper Mill, Frenchtown, Montana

## Introduction

In a letter dated January 9, 1985, the Regional Administrator (Region VIII) received a request for assistance from the Department of Health and Environmental Sciences, State of Montana for use of a mobile bioassay facility to conduct a long term test using eggs of rainbow trout, on treated wastewater from Champion International paper mill. Assistance was requested to conduct long-term chronic bioassays using trout eggs through post hatch.

For some time, there has been public concern about water quality in the lower Clark Fork River, in particular the long-term impacts from the discharge of treated wastewater from Champion International at Frenchtown. The question that needs resolution is whether the Champion wastewater has discernable effects on the early-life stages of trout inhabiting the Clark Fork River. Results of such a study would aid in the review of a modified discharge permit issued by the State of Montana in April 1984.

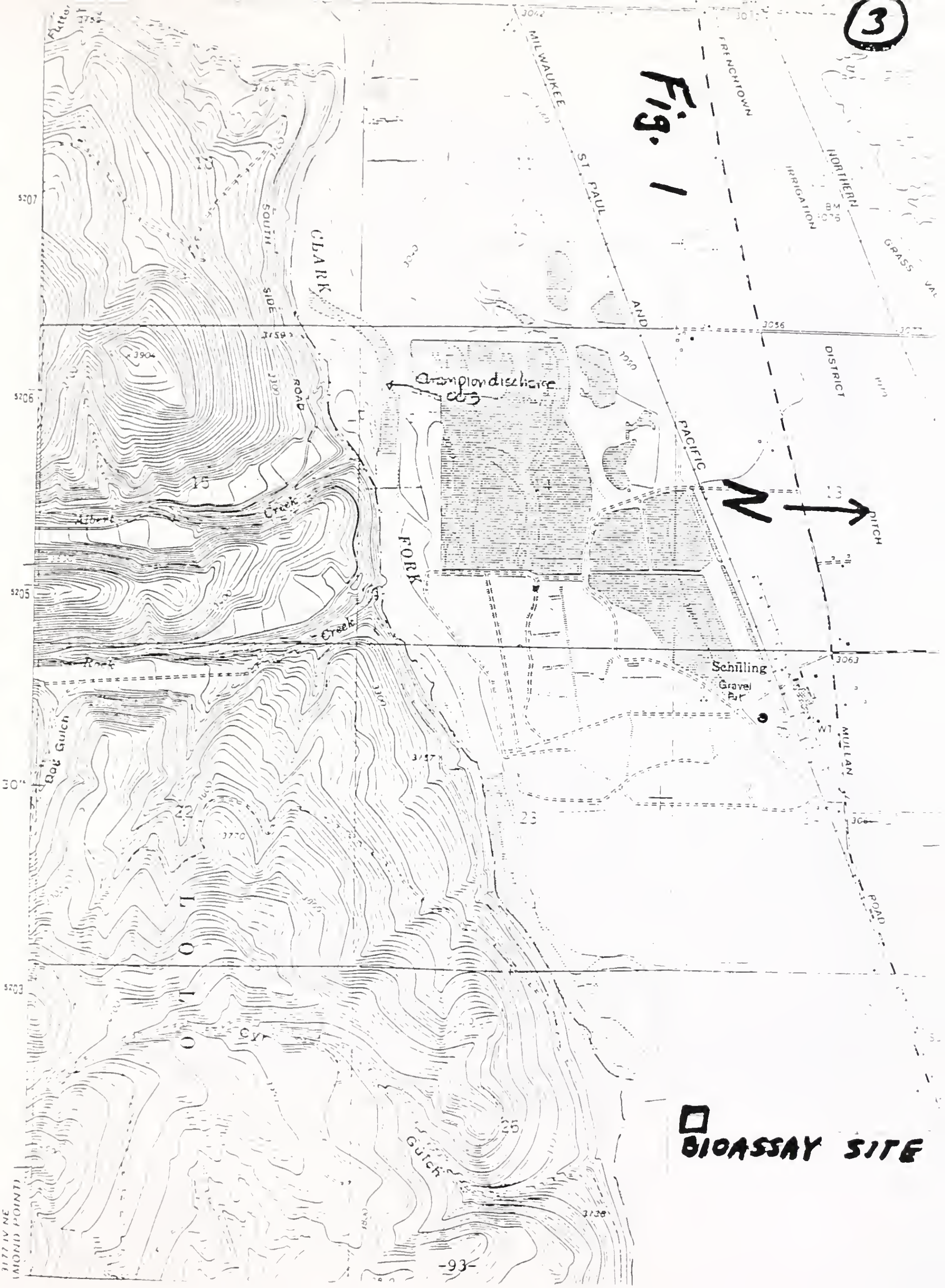
## Background of the Study

The Champion International Paper Mill, formerly Hoerner-Waldorf, located at Frenchtown, Montana began operation in 1957. At startup, mill production of unbleached kraft pulp totalled 250 tons/day (TPD). Since 1957, mill expansions have occurred in 1960, 1966, 1970, and 1976; with the current production, a maximum of 2005 TPD unbleached kraft pulp and liner board. At present, Champion wastewater receives the equivalent of secondary treatment (aeration) followed by a minimum of 10 days retention. An intricate and convoluted series of retention ponds is shown by diagram in Figure I. Three non-chloro-phenolic biocides are used to treat the paper machine stock systems and the minimum amount of dilution the wastewater would receive in the Clark Fork River is 200 parts river water to 1 part wastewater. A more detailed explanation follows concerning issues in the Clark Fork.

According to the publication, Montana Water Quality 1984, the two largest dischargers to the lower Clark Fork are the City of Missoula and Champion International. Both have been asked to expand their self-monitoring programs to provide data needed by the state to assess water quality impacts. A modified permit, issued in April 1984, allows Champion to increase its yearly load of suspended solids to the river and to discharge year-round, but only when flows in the river exceed 1,900 cubic feet per second (cfs). Nutrients, heavy metals and suspended solids, especially organic solids also are of concern. Concern has been expressed about Champion and the City of Missoula as point sources of nitrogen and phosphorus which may stimulate undesirable algal growth in downstream reservoirs and in Lake Pend Oreille, Idaho. Heavy metals which originate upstream in the Butte mining district, may be mobilized by lowered dissolved oxygen and lower pH of bottom waters downstream thereby making them more toxic to fish and aquatic life.

③

Fig. 1



Anaconda discharge
N
BIOASSAY SITE
CLARK FORK
SOUTH SIDE ROAD
MILWAUKEE ST. PAUL AND PACIFIC
FRENCHTOWN IRRIGATION DISTRICT
NORTHERN GRASS VALLEY DITCH
MULLAN ROAD
Schilling Gravel Pit
Albert Creek
Rock Creek
Dog Gulch
Gulch
LO LO
3904
3056
3063
57'30"
15
14
13
22
23
25

## Request for Assistance

The request from the State of Montana involved testing the long term effects of wastewater using two options:

1. a 30-day test from fertilized trout eggs to hatch, or
2. a 60-day test from the eyed-egg stage of a trout through 30 days of growth.

According to the letter of request, the first option has the advantage of testing at what is believed to be the most sensitive stage of embyological development, the period immediately after fertilization. The second option allows for measurement of rate of growth and survival, two sensitive endpoints. Because the American Society of Testing and Materials Procedure (ASTM) recommends the eggs should be incubated at 12°C and at extremely low light intensity, the development of eggs using either option is extremely lengthy.

## Test Procedure and Conditions

The Montana Department of Health and Environmental Sciences has requested that tests be conducted on the most sensitive stages of fish inhabiting the Clark Fork River. Specifically, tests were requested using the egg stage of the rainbow trout life cycle. Wastes from the pulp mill lagoon system are to be mixed with dilution water from the Clark Fork River and pumped through a "flow-through" dilution system to test chambers containing trout eggs. However, information received from Dr. C.E. Warren at Oregon State University (Personal Communication 2-4-85) indicates that the most sensitive stage of a salmonid exposed to stable unbleached kraft pulp mill waste, is the period from button-up stage to the juvenile stage in the life cycle.

Therefore, EPA Region VIII personnel propose the following tests. Rainbow trout, just after the button-up stage (on feed), will be exposed to dilutions of mill waste for approximately 30 days. Waste dilutions will range from 1:10 to 1:1000 with median dilution present at 1:200 dilution of wastewater to dilution water. Major endpoints of the study will be mortality and growth rates of the larvae. Larvae will be fed four times/day at a relatively high rate of food consumption (>4% diet dry weight/fish weight/day) as suggested in the proposed ASTM methods for chronic tests with salmonid fish. Test temperatures will be held at 12°C ± 1.5° throughout the test period. The test species will be rainbow trout, *Salmo gairdneri*. Larval fish will be obtained from the U.S. Fish and Wildlife hatchery located at Creston, Montana. A seven-day *Ceriodaphnia* life cycle test will be conducted in parallel with the rainbow trout study using samples from the dilutions used in the trout study. In addition a 7-day *Ceriodaphnia* life cycle test will be used to test ambient stream conditions in the Clak Fork River at eight sites above and below Champion International. The locations selected are those in which algal assays are being conducted by EPA/Corvallis as part of the Water Quality Bureau's Lower Clark Fork River Study.

| Station Number | Location |
|---|---|
| 11 | CFR above Missoula WWTP |
| 12 | CFR at Harper Bridge (above Champion) |
| 13 | CFR at Huson (below Champion) |
| 14 | CFR at Superior |
| 15 | CFR above Flathead River confluence |
| 16 | CFR above Thompson Falls Reservoir |
| 17 | CFR below Thompson Falls Dam |
| 18 | CFR below Noxon Dam |

## Project Description

Study Location - The Champion Paper Mill is located about 20 miles northwest of Missoula, Montana near Frenchtown. The mill and waste ponds are located on the left side of the river (north bank) with some ponds close enough to the river to seep wastes into the river. The mobile laboratory will be located on mill property at a power source located upstream of ponds 1A and 2 (Figure 1). Treated wastewater will be hauled (daily) to the mobile laboratory and tested in two ways. Using one diluter system, wastewater will be mixed with Clark Fork River water obtained at the site (upstream of the mill).

In a second separate diluter system, wastewater will be diluted with unchlorinated well water (used for processing at the mill). The well water will be pumped daily to the mobile laboratory. Using two sources of dilution water should aid in the interpretation of results from the trout studies and the wastewater.

Dates of Testing - The test is scheduled from May 4th through June 3rd. Allowing for set-up and breakdown time, we estimate actual on-site time would be from May 1st through June 6th.

Reference Methodologies - All test procedures will follow the EPA "Methods of Measuring the Acute Toxicity of Effluents to Aquatic organisms", 2nd edition and 3rd edition (draft). However, because this is a chronic study, guidance for the the test will be ASTMs "Proposed New Standard Practice for Conducting Fish Early Life-Stage Toxicity Tests (draft No. 8). In addition, methods listed in Birge and Blacks "*In Situ* Acute/Chronic Toxicological Monitoring of Industrial Effluents for NPDES Biomonitoring Program Using Fish and Amphibian Embryo-Larval Stages as Test Organisms" (EPA Report No. DWEP-82-001), and Short-Term Embryo-Larval Test for Effluent Biomonitoring (Preliminary Draft; available from T.H. Morgan School of Biological Sciences, University of Kentucky, Lexington, KT 40506. Methods for the *Ceriodaphnia* testing will be those of Mount and Norberg (1984), with analysis of data following the procedures of Hamilton, M.A. 1984. Statistical Analysis of the Seven-day *Ceriodaphnia reticulata* Reproductivity Toxicity Test. Contract Order No. J3905 NASX-1, U.S. EPA Duluth, MN.

Sampling Dates and Parameters - Sets of "grab" samples will be collected from each of 14 aquaria according to the schedule in Table 1.

Table 1. Sample Parameters and Frequency Champion International Paper Mill, Frenchtown, Montana

| Analysis | Frequency | Lab Location |
|---|---|---|
| Dissolved Sulfide | Weekly | State |
| D.O. | Daily | Mobile Lab |
| Temp. | Continuous | Mobile Lab |
| Hardness[1] | Twice Weekly | State |
| Alkalinity | Daily | Mobile Lab |
| pH | Daily | Mobile Lab |
| ~~TDS~~[1] | Daily | Mobile Bioassay |
| Conductivity | ~~Weekly~~ | ~~State~~ |
| NH3-N | Weekly | State |
| Dissolvent Organic Carbon | Weekly | State |
| Total Organic Carbon | Weekly | State |
| BOD | Weekly | ~~State~~ Champion |
| Color | Weekly | ~~State~~ Champion |
| Chlorides | Weekly | State |
| ~~Sulfide~~ | ~~Weekly~~ | ~~State~~ |
| ICAP Metals | 8 Samples | Denver-EPA |
| Organic Priority Pollutants | 8 Samples | Denver-EPA |

[1] - Frequency may be increased due to unusual hydrologic conditions.

[illegible]

[illegible]

Conductivity
TOC
BOD
Chlorides

[illegible]

[illegible] : Color & BOD
State: Dissolved [illegible]
— Hardness
— Conductivity
$NH_3$-N
Dissolved Organic Carbon
Total Organic Carbon
— Chlorides

## Sample Collection, Handling, Preservation

All sample collection, handling and preservation will follow the guidelines established in "a Guide for Field Samples", "Methods for Chemical Analysis of Water and Wastes, and "Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents". Information regarding sample size, container, preservative and special handling for parameters under consideration is summarized in Table 2.

## Table 2

Sample Requirements for Chemical Samples Sent to the State and EPA Laboratories

| Chemical | Sample Size | Container | Preservative |
|---|---|---|---|
| $NH_3$-N, Total<br>$NO_3$-N<br>$NO_2$-N | 1 liter | Cubitainer | 2ml conc $H_2SO_4$ |
| TDS or Conductivity and Hardness | 1 liter | Cubitainer | Chilled |
| Priority Pollutant Organics | 1 quart | Glass Jar | Chilled |
| ICAP-Metals | 1 quart | Cubitainer | 5ml conc. $HNO_3$ |

State supplies this

## Quality Assurance

All direct reading bioassay laboratory equipment will be checked for calibration before each series of samples are collected. In addition, each test concentration is run in duplicate and a control (0% waste) is run at the same time. Samples of various waste concentrations from select aquaria will be split with the State lab and the EPA mobile lab. When the mobile laboratory is set-up on site, each diluter will be checked and recalibrated to deliver the required amounts of effluent or dilution water to each aquarium. At the end of the test a representative number of fish from each test conc. will be weighed, measured and checked for abnormalities. At least one duplicate priority pollutant and ICAP sample once during the study will be tak

## Personnel Needs

Personnel from EPA (Bruce Binkley [NEIC], Jim Lazorchak, Denise Link and Del Nimmo [WMD]) will conduct the trout and Ceriodaphnia studies. In addition, Gary Ingman from the State Department of Health and Environmental Sciences will assist in the project and be the primary contact with Champion International.

## Record Keeping

Sample tags shall be affixed to each sample container. Tags shall be legible and filled out using ball-point or other permanent marking pen. Information to be entered on each tag shall include:

1. Sample identification number
2. Date and time for collection
3. Name of source, type of sample
4. Appropriate field measurements (pH, temperature, etc.)
5. Analyses to be performed
6. Preservative(s) used
7. Size of sample
8. Name of person collecting sample
9. Witness to the collection, if appropriate

Lab request sheets will accompany all samples. A bound field notebook will be maintained by the survey leader to provide a daily record of events pertaining to the study. All members of the survey party will provide input to the survey leaders field notebook. Notes entered into the field notebook should be kept complete and permanent.

Information regarding calibration of field instrumentation shall be entered into the field notebook or logbook specifically provided for the purpose.

## Report

A report of the findings will be prepared upon completion of field and laboratory work. Reports may be prepared as appropriate to call attention to significant findings. Data will be entered into STORET. Del Nimmo will be responsible for data reduction, analyses, and preparing the report. An initial draft report will be prepared within 60 days of completion of all tests.

Any question regarding this plan can be addressed to C. Runas, Del Nimmo (293-1579) or L. Parrish (236-5084)

Cost Estimate

| | |
|---|---|
| Per diem for (for 6 weeks 2 staff persons) | $ 3,600 |
| Overtime (40 hrs/person) | 1,300 |
| Misc. Supplies | 300 |
| Air Freight | 150 |
| Rental Car | 500 |
| Gas for the rental car | 200 |
| Total | $ 6,150 |

Equipment Needs

Table 3 summarizes the equipment and supplies required for the testing.

# Table 3

## Equipment List - Bioassay

Mobile Bioassay Lab
Another Support Vehicle
Pumps
Hose
Extension cords
pH meters - 2 plus standards
Dissolved Oxgen meters - 2
Thermometers - 2
Tygon Tubing - 1/4", 3/8", 1/2", 5/8"
Plastic Buret - Dissolved Oxygen
Ring Stand
D.O. powder pillows
~~Ammonia meter~~
~~Standard ammonia solutions~~
Balance
Weighing boats
$H_2SO_4$
Disposable pipettes
Ice chests
~~Fish food~~
Cubitainers
$HNO_3$
Specific Conductance Meter

# Means ($\bar{x}$) of Chemical Constituents — Champion International Study — Dilutions of River Water

| Percentage Wastewater Dilution | Total NH3 mg/l | | Temp C | | pH | | Dissolv. Sulfide mg/l | | DOC[1] mg/l | | TOC mg/l | | Conductivity μmhos/cm | | Dissolv. Oxygen mg/l | | Ca mg/l | | Mg mg/l | | Alkalinity mg/l as $CaCO_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 |
| 0 | 0.09 | — | 12 | 12 | 7.2 | 7.1 | 0.06 | — | 2.8 | — | 3.7 | — | 135 | 131 | 7.9 | 7.8 | 17.5 | — | 3.9 | — | 57.6 | 56.3 |
| 0.2 | 0.16 | — | 12 | 11 | 7.1 | 7.1 | <0.05 | — | — | — | 4.3 | — | 134 | 134 | 7.5 | 7.5 | 17.4 | — | 4.0 | — | 52.1 | 56.0 |
| 0.36 | 0.12 | — | 12 | 12 | 7.1 | 7.1 | 0.09 | — | 2.0 | — | 5.9 | — | 140 | 140 | 7.8 | 7.7 | 17.1 | — | 4.1 | — | 53.4 | 57.6 |
| 0.64 | 0.18 | — | 12 | 12 | 7.1 | 7.1 | 0.10 | — | 4.6 | — | 5.4 | — | 147 | 147 | 7.4 | 7.7 | 17.8 | — | 4.1 | — | 57.1 | 58.8 |
| 1.12 | 0.20 | — | 12 | 12 | 7.1 | 7.1 | 0.11 | — | 4.8 | — | 5.9 | — | 159 | 160 | 7.5 | 7.6 | 17.8 | — | 4.1 | — | 57.6 | 61.3 |
| 1.5 | 0.17 | — | 12 | 12 | 7.1 | 7.1 | 0.12 | — | 5.6 | — | 6.9 | — | 170 | 171 | 7.7 | 7.4 | 17.8 | — | 4.1 | — | 60.0 | 63.0 |
| 2.0 | 0.13 | — | 13 | 12 | 7.1 | 7.1 | 0.12 | — | 6.1 | — | 7.3 | — | 185 | 187 | 7.7 | 7.5 | 17.9 | — | 4.3 | — | 59.1 | 65.9 |

[1] Single sample on a single replicate

ATTACHMENT C

# Means ($\bar{x}$) of Chemical Constituents – Champion International Study – Dilutions of Well Water

| Percentage Wastewater Dilution | Total $NH_3$ mg/l | | Temp C | | pH | | Dissolv. Sulfide mg/l | | DOC[1] mg/l | | TOC mg/l | | Conductivity µmhos/cm | | Dissolv. Oxygen mg/l | | Ca mg/l | | Mg mg/l | | Alkalinity mg/l as $CaCO_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 | Rep1 | Rep2 |
| 0 | 0.03 | — | 12 | 12 | 7.5 | 7.5 | <0.05 | — | 0.8 | — | 2.2 | — | 284 | 279 | 7.6 | 7.5 | 39.1 | — | 10.4 | — | 115.2 | 124.3 |
| 0.2 | 0.16 | — | 12 | 11 | 7.3 | 7.4 | <0.05 | — | 1.6 | — | 2.0 | — | 278 | 285 | 7.5 | 7.2 | 39.1 | — | 10.2 | — | 116.8 | 124.1 |
| 0.36 | — | — | 12 | 11 | 7.4 | 7.4 | <0.05 | — | 1.3 | — | 2.6 | — | 285 | 289 | 7.7 | 7.3 | 38.9 | — | 10.4 | — | 116.1 | 123.1 |
| 0.64 | 0.11 | — | 12 | 11 | 7.4 | 7.4 | <0.05 | — | 1.9 | — | 2.4 | — | 288 | 293 | 7.4 | 7.3 | 39.2 | — | 10.5 | — | 118.1 | 126.1 |
| 1.12 | 0.11 | — | 12 | 11 | 7.4 | 7.5 | <0.05 | — | 2.0 | — | 3.2 | — | 303 | 304 | 7.6 | 7.6 | 39.7 | — | 10.4 | — | 119.3 | 127.2 |
| 1.5 | 0.12 | — | 12 | 11 | 7.4 | 7.5 | <0.05 | — | 2.5 | — | 4.0 | — | 312 | 312 | 7.6 | 7.5 | 39.7 | — | 10.5 | — | 119.2 | 125.6 |
| 2.0 | 0.16 | — | 12 | 11 | 7.4 | 7.5 | <0.05 | — | 2.4 | — | 4.6 | — | 323 | 327 | 7.5 | 7.2 | 39.5 | — | 10.3 | — | 122.5 | 129.1 |

[1] Single sample on a single replicate

Note: Sample was incorrectly labeled in lab as Silver Bow; was actually Champion Wastewater

FRN 9371

Sample Number
CHAMPION WASTE
5-17-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-18-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 5-29-85
DATE ANALYZED: 6-10-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 200

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6-trichlorophenol | <10 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2-chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2-nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxyl) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | <10 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | |
| (67B) | 85-68-7 | benzyl butyl phthalate | |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | |
| (71B) | 131-11-3 | dimethyl phthalate | |
| (72B) | 56-55-3 | benzo(a)anthracene | |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

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FRN 9371

Environmental Protection Agency, CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313 703/557-2490

**Sample Number**
CHAMPION WASTE
5-17-85

## Organics Analysis Data Sheet
(Page 3)

### Pesticide/PCBs

Concentration: [✓ Low] Medium (Circle One)
Date Extracted/Prepared: 5-29-85
Date Analyzed: 6-10-85
[✓ Conc]/Dil Factor: 200

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | <10 |
| 319-85-7 | Beta-BHC | │ |
| 319-86-8 | Delta-BHC | │ |
| 58-89-9 | Gamma-BHC (Lindane) | │ |
| 76-44-8 | Heptachlor | │ |
| 309-00-2 | Aldrin | │ |
| 1024-57-3 | Heptachlor Epoxide | │ |
| 959-98-8 | Endosulfan I | │ |
| 60-57-1 | Dieldrin | │ |
| 72-55-9 | 4,4'-DDE | │ |
| 72-20-8 | Endrin | │ |
| 33213-65-9 | Endosulfan II | │ |
| 72-54-8 | 4,4'-DDD | │ |
| 7421-93-4 | Endrin Aldehyde | │ |
| 1031-07-8 | Endosulfan Sulfate | │ |
| 50-29-3 | 4,4'-DDT | │ |
| 72-43-5 | Methoxychlor | │ |
| 53494-70-5 | Endrin Ketone | │ |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12674-11-2 | Aroclor-1016 | │ |
| 11104-28-2 | Aroclor-1221 | │ |
| 11141-16-5 | Aroclor-1232 | │ |
| 53469-21-9 | Aroclor-1242 | │ |
| 12672-29-6 | Aroclor-1248 | │ |
| 11097-69-1 | Aroclor-1254 | │ |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)
$V_s$ = Volume of water extracted (ml)
$W_s$ = Weight of sample extracted (g)
$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form 1 4/84

Form I. (continued).

CHAMPION WASTE

5-17-85

# Organics Analysis Data Sheet
(Page 4)

## Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | [✓ RT] or Scan Number | Estimated Concentration ([✓ ug/l] or ug/kg) |
|---|---|---|---|---|
| 1. | 1[2-(2-METHOXY-1-METHYLETHOXY)-1- | A/B/N | 16.53 | 480 |
| ~~2.~~ | METHYLETHOXY]-2-PROPANOL $C_{10}H_{22}O_4$ | | | |
| ~~3.~~ 2 | ISOMER OF #1 | | 16.90 | 145 |
| ~~4.~~ 3 | METHYLPENTADECANOIC ACID | | 26.82 | 188 |
| ~~5.~~ 4 | ANDROST-16-EN-3-ONE | | 26.98 | 99.5 |
| ~~6.~~ 5 | 1-EICOSENE $C_{20}H_{40}$ MW 280 | | 30.73 | 164 |
| ~~7.~~ 6 | ISOPIMARIC ACID MW 302 | | 31.30 | 216 |
| ~~8.~~ 7 | PIMARIC ACID MW 302 | | 31.77 | 804 |
| ~~9.~~ 8 | SIMILAR TO PIMARIC ACID MW 302 | | 32.52 | 1050 |
| ~~10.~~ 9 | DEHYDROABIETIC ACID MW 300 | | 32.97 | 1120 |
| ~~11.~~ 10 | 15-HYDROXY-ANDROST-4-ENE-3 17-DIONE | | 33.42 | 538 |
| ~~12.~~ 11 | UNKNOWN ACID MW 340 | | 33.75 | 336 |
| ~~13.~~ 12 | 1-TETRACOSANOL $C_{24}H_{50}O$ | | 34.95 | 171 |
| ~~14.~~ 13 | ERGOST-5-EN-3-OL $C_{28}H_{48}O$ MW 400 | | 41.72 | 243 |
| ~~15.~~ 14 | STIGMAST-5-EN-3-OL $C_{29}H_{50}O$ MW 414 | ↓ | 43.65 | 847 |
| | | | | |
| 17. | | | | |
| 18. | | | | |
| 19. | | | | |
| 20. | | | | |
| 21. | | | | |
| 22. | | | | |
| 23. | | | | |
| 24. | | | | |
| 25. | | | | |
| 26. | | | | |
| 27. | | | | |
| 28. | | | | |
| 29. | | | | |
| 30. | | | | |

NATURAL ACIDS, KETONES AND ALCOHOLS.

Note: Sample was mislabeled in lab as Silver Bow; was Clark Fork at Champion.

FRN 9362

Sample Number
CHAMPION RIVER
5-17-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-17-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 5-29-85
DATE ANALYZED: 6-7-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 1000

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6- trichlorophenol | < 2 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2- chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2- nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxy) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | < 2 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | |
| (67B) | 85-68-7 | benzyl butyl phthalate | |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | ↓ |
| (71B) | 131-11-3 | dimethyl phthalate | 2.0 |
| (72B) | 56-55-3 | benzo(a)anthracene | < 2 |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

Environmental Protection Agency   CLP Sample Management Office
P.O. Box 818   Alexandria, Virginia 22313   703/557-2490

FRN 9362

**Sample Number**
CHAMPION RIVER
5-17-85

## Organics Analysis Data Sheet
(Page 3)

### Pesticide/PCBs

Concentration: [✓ Low] Medium (Circle One)

Date Extracted/Prepared: 5-29-85

Date Analyzed: 6-7-85

[✓ Conc]/Dil Factor: 1000

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | <2 |
| 319-85-7 | Beta-BHC | │ |
| 319-86-8 | Delta-BHC | │ |
| 58-89-9 | Gamma-BHC (Lindane) | │ |
| 76-44-8 | Heptachlor | │ |
| 309-00-2 | Aldrin | │ |
| 1024-57-3 | Heptachlor Epoxide | │ |
| 959-98-8 | Endosulfan I | │ |
| 60-57-1 | Dieldrin | │ |
| 72-55-9 | 4,4'-DDE | │ |
| 72-20-8 | Endrin | │ |
| 33213-65-9 | Endosulfan II | │ |
| 72-54-8 | 4,4'-DDD | │ |
| 7421-93-4 | Endrin Aldehyde | │ |
| 1031-07-8 | Endosulfan Sulfate | │ |
| 50-29-3 | 4,4'-DDT | │ |
| 72-43-5 | Methoxychlor | │ |
| 53494-70-5 | Endrin Ketone | │ |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12574-11-2 | Aroclor-1016 | │ |
| 11104-29-2 | Aroclor-1221 | │ |
| 11141-16-5 | Aroclor-1232 | │ |
| 53469-21-9 | Aroclor-1242 | │ |
| 12672-29-6 | Aroclor-1248 | │ |
| 11097-69-1 | Aroclor-1254 | │ |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)

$V_s$ = Volume of water extracted (ml)

$W_s$ = Weight of sample extracted (g)

$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form 1   4/84

Form I. (continued).

Note: lab incorrectly labeled sample as Silver Bow; it is actually Champion Well.

FRN 9363

Sample Number
CHAMPION WELL
5-17-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-17-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 5-29-85
DATE ANALYZED: 6-7-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 1000

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6-trichlorophenol | <2 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2-chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2-nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxy) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | <2 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | |
| (67B) | 85-68-7 | benzyl butyl phthalate | |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | |
| (71B) | 131-11-3 | dimethyl phthalate | |
| (72B) | 56-55-3 | benzo(a)anthracene | |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

Environmental Protection Agency CLP Sample Management Office
P.O. Box 818 Alexandria Virginia 22313 703/557-2490

FRN 9363

**Sample Number**
CHAMPION WELL

5-17-85

# Organics Analysis Data Sheet
(Page 3)

## Pesticide/PCBs

Concentration: [✓ Low] Medium (Circle One)

Date Extracted/Prepared: 5-29-85

Date Analyzed: 6-7-85

[✓ Conc]/Dil Factor: 1000

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | < 2 |
| 319-85-7 | Beta-BHC | |
| 319-86-8 | Delta-BHC | |
| 58-89-9 | Gamma-BHC (Lindane) | |
| 76-44-8 | Heptachlor | |
| 309-00-2 | Aldrin | |
| 1024-57-3 | Heptachlor Epoxide | |
| 959-98-8 | Endosulfan I | |
| 60-57-1 | Dieldrin | |
| 72-55-9 | 4,4'-DDE | |
| 72-20-8 | Endrin | |
| 33213-65-9 | Endosulfan II | |
| 72-54-8 | 4,4'-DDD | |
| 7421-93-4 | Endrin Aldehyde | |
| 1031-07-8 | Endosulfan Sulfate | |
| 50-29-3 | 4,4'-DDT | |
| 72-43-5 | Methoxychlor | |
| 53494-70-5 | Endrin Ketone | |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12674-11-2 | Aroclor-1016 | |
| 11104-28-2 | Aroclor-1221 | |
| 11141-16-5 | Aroclor-1232 | |
| 53469-21-9 | Aroclor-1242 | |
| 12672-29-6 | Aroclor-1248 | |
| 11097-69-1 | Aroclor-1254 | |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)

$V_s$ = Volume of water extracted (ml)

$W_s$ = Weight of sample extracted (g)

$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form I. (continued).

ENVIRONMENTAL PROTECTION AGENCY
REGION VIII, DENVER, COLORADO

# LABORATORY SERVICES REQUEST

Page 9

PROJECT NAME [illegible] PROJECT CODE ______ SAMPLES COLL. BY [illegible] DATE [illegible]

SAMPLES RECEIVED AT LABORATORY BY ______ DATE ______ DATA REVIEWED BY ______

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| STATION CODE | | Sample taken | Sample taken | Sample tak | | | |
| SAMPLE COLL. TIME | | 5/31/85 | 5/31/85 | 5/31/85 | [illegible] | [illegible] | [illegible] |
| STATION DESCRIPTION AND REMARKS | [illegible] | [illegible] well<br>SA 11 | well water<br>SA 4 | Clark Fork [illegible]<br>SA 3 | [illegible]<br>SA-1 | [illegible] River (Clark Fork<br>SA 2 | Champion [illegible]<br>SA-3 |
| CODE | PARAMETER | | | | | | |
| | [illegible] | | | | | | |
| | [illegible] mg/l | <5 | <5 | <5 | <5 | <5 | <5 |
| | [illegible] | <5 | <5 | <5 | <5 | <5 | <5 |
| | [illegible] | 57 | <10 | <10 | <10 | <10 | 73 |
| | [illegible] | 36 | <5 | 10 | <5 | 10 | 59 |
| | [illegible] | <100 | <100 | <100 | <100 | <100 | <100 |
| | [illegible] mg/l | 50.0 | 30.5 | 17.4 | 36.8 | 15.5 | 47.4 |
| | Mg mg/l | 10.3 | 11.0 | 5.0 | 11.1 | 5.5 | 12.7 |
| | [illegible] mg/l | 465 | 4.3 | 3.0 | 9.0 | 3.6 | 531 |

MAX HOLD TIME | TAG COLOR SYMBOL

All results in mg/l unless otherwise indicated, pH in units, turbidity in JTU, specific conductance in µmhos/cm, as per STORET.

☆ GPO 1979-680-570

R8EPA-012

Note: sample [illegible] designated as Silver Bow
should be Clark Fork River at Champion

FRN 9366

Sample Number
CHAMPION
5-31-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-31-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 6-5-85
DATE ANALYZED: 6-7-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 1000

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6-trichlorophenol | <2 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2-chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2-nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxy) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | <2 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | |
| (67B) | 85-68-7 | benzyl butyl phthalate | |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | |
| (71B) | 131-11-3 | dimethyl phthalate | |
| (72B) | 56-55-3 | benzo(a)anthracene | |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

Environmental Protection Agency CLP Sample Management Office
P O Box 818 Alexandria, Virginia 22313 703/557-2490

FRN 9366

| Sample Number |
|---|
| CHAMPION |

5-31-85

## Organics Analysis Data Sheet
(Page 3)

### Pesticide/PCBs

Concentration [✓ Low] Medium (Circle One)

Date Extracted/Prepared 6-5-85

Date Analyzed 6-7-85

[✓ Conc]/Dil Factor 1000

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | <2 |
| 319-85-7 | Beta-BHC | |
| 319-86-8 | Delta-BHC | |
| 58-89-9 | Gamma-BHC (Lindane) | |
| 76-44-8 | Heptachlor | |
| 309-00-2 | Aldrin | |
| 1024-57-3 | Heptachlor Epoxide | |
| 959-98-8 | Endosulfan I | |
| 60-57-1 | Dieldrin | |
| 72-55-9 | 4,4'-DDE | |
| 72-20-8 | Endrin | |
| 33213-65-9 | Endosulfan II | |
| 72-54-8 | 4,4'-DDD | |
| 7421-93-4 | Endrin Aldehyde | |
| 1031-07-8 | Endosulfan Sulfate | |
| 50-29-3 | 4,4'-DDT | |
| 72-43-5 | Methoxychlor | |
| 53494-70-5 | Endrin Ketone | |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12674-11-2 | Aroclor-1016 | |
| 11104-28-2 | Aroclor-1221 | |
| 11141-16-5 | Aroclor-1232 | |
| 53469-21-9 | Aroclor-1242 | |
| 12672-29-6 | Aroclor-1248 | |
| 11097-69-1 | Aroclor-1254 | |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)

$V_s$ = Volume of water extracted (ml)

$W_s$ = Weight of sample extracted (g)

$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form 1 4 84

Form I. (continued).

[illegible] sample identified should have
been as Champion well water

FRN 9369

Sample Number
CLARK FORK WELL
5-31-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-31-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 6-5-85
DATE ANALYZED: 6-10-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 1000

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6-trichlorophenol | <2 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2-chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2-nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxy) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | <2 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | ↓ |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | 36.1 |
| (67B) | 85-68-7 | benzyl butyl phthalate | <2 |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | |
| (71B) | 131-11-3 | dimethyl phthalate | |
| (72B) | 56-55-3 | benzo(a)anthracene | |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

1983

Environmental Protection Agency. CLP Sample Management Office
P O Box 818, Alexandria, Virginia 22313 703/557-2490

FRN 9369

**Sample Number**
CLARK FORK WELL
5-31-85

## Organics Analysis Data Sheet
(Page 3)

### Pesticide/PCBs

Concentration: [✓ Low] Medium (Circle One)

Date Extracted/Prepared: 6-5-85

Date Analyzed 6-10-85

[✓ Conc]/Dil Factor: 1000

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | <2 |
| 319-85-7 | Beta-BHC | |
| 319-86-8 | Delta-BHC | |
| 58-89-9 | Gamma-BHC (Lindane) | |
| 76-44-8 | Heptachlor | |
| 309-00-2 | Aldrin | |
| 1024-57-3 | Heptachlor Epoxide | |
| 959-98-8 | Endosulfan I | |
| 60-57-1 | Dieldrin | |
| 72-55-9 | 4,4'-DDE | |
| 72-20-8 | Endrin | |
| 33213-65-9 | Endosulfan II | |
| 72-54-8 | 4,4'-DDD | |
| 7421-93-4 | Endrin Aldehyde | |
| 1031-07-8 | Endosulfan Sulfate | |
| 50-29-3 | 4,4'-DDT | |
| 72-43-5 | Methoxychlor | |
| 53494-70-5 | Endrin Ketone | |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12674-11-2 | Aroclor-1016 | |
| 11104-28-2 | Aroclor-1221 | |
| 11141-16-5 | Aroclor-1232 | |
| 53469-21-9 | Aroclor-1242 | |
| 12672-29-6 | Aroclor-1248 | |
| 11097-69-1 | Aroclor-1254 | |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)

$V_s$ = Volume of water extracted (ml)

$W_s$ = Weight of sample extracted (g)

$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form 1 4 84

Form I. (continued).

Note: Sample was mislabeled as Silver Bow; was actually Champion wastewater

FRN 9372

Sample Number
CHAMPION WASTE
5-31-85

## ORGANICS ANALYSIS DATA SHEET

Laboratory Name: USEPA REGION 8
Lab Sample ID No: SILVER BOW
Sample Matrix: AQUEOUS
Data Release Authorized By: A. CURTIS

Case No: —
QC Report No:
Contract No.:
Date Sample Received: 5-31-85

### SEMIVOLATILE COMPOUNDS

CONCENTRATION: [✓ LOW] MEDIUM HIGH (circle one)
DATE EXTRACTED/PREPARED: 6-5-85
DATE ANALYZED: 6-10-85
PERCENT MOISTURE: —
[✓ CONC.]/DILUTION FACTOR: 200

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (21A) | 88-06-2 | 2,4,6-trichlorophenol | <2 |
| (22A) | 59-50-7 | p-chloro-m-cresol | |
| (24A) | 95-57-8 | 2-chlorophenol | |
| (31A) | 120-83-2 | 2,4-dichlorophenol | |
| (34A) | 105-67-9 | 2,4-dimethylphenol | |
| (57A) | 88-75-5 | 2-nitrophenol | |
| (58A) | 100-02-7 | 4-nitrophenol | |
| (59A) | 51-28-5 | 2,4-dinitrophenol | |
| (60A) | 534-52-1 | 4,6-dinitro-2-methylphenol | |
| (64A) | 87-86-5 | pentachlorophenol | |
| (65A) | 108-95-2 | phenol | |
| | 65-85-0 | benzoic acid | |
| | 95-48-7 | 2-methylphenol | |
| | 108-39-4 | 4-methylphenol | |
| | 95-95-4 | 2,4,5-trichlorophenol | |
| (1B) | 83-32-9 | acenaphthene | |
| (5B) | 92-87-5 | benzidine | |
| (8B) | 120-82-1 | 1,2,4-trichlorobenzene | |
| (9B) | 118-74-1 | hexachlorobenzene | |
| (12B) | 67-72-1 | hexachloroethane | |
| (18B) | 111-44-4 | bis(2-chloroethyl)ether | |
| (20B) | 91-58-7 | 2-chloronaphthalene | |
| (25B) | 95-50-1 | 1,2-dichlorobenzene | |
| (26B) | 541-73-1 | 1,3-dichlorobenzene | |
| (27B) | 106-46-7 | 1,4-dichlorobenzene | |
| (28B) | 91-94-1 | 3,3'-dichlorobenzidine | |
| (35B) | 121-14-2 | 2,4-dinitrotoluene | |
| (36B) | 606-20-2 | 2,6-dinitrotoluene | |
| (37B) | 122-66-7 | 1,2-diphenylhydrazine | |
| (39B) | 206-44-0 | fluoranthene | |
| (40B) | 7005-72-3 | 4-chlorophenyl phenyl ether | |
| (41B) | 101-55-3 | 4-bromophenyl phenyl ether | |
| (42B) | 39638-32-9 | bis (2-chloroisopropyl) ether | |
| (43B) | 111-91-1 | bis (2-chloroethoxy) methane | ↓ |

| PP # | CAS # | | [✓ ug/l] or ug/kg (circle one) |
|---|---|---|---|
| (52B) | 87-68-3 | hexachlorobutadiene | <2 |
| (53B) | 77-47-4 | hexachlorocyclopentadiene | |
| (54B) | 78-59-1 | isophorone | |
| (55B) | 91-20-3 | naphthalene | |
| (56B) | 98-95-3 | nitrobenzene | |
| (61B) | 62-75-9 | N-nitrosodimethylamine | |
| (62B) | 86-30-6 | N-nitrosodiphenylamine | |
| (63B) | 621-64-7 | N-nitrosodipropylamine | |
| (66B) | 117-81-7 | bis (2-ethylhexyl) phthalate | |
| (67B) | 85-68-7 | benzyl butyl phthalate | |
| (68B) | 84-74-2 | di-n-butyl phthalate | |
| (69B) | 117-84-0 | di-n-octyl phthalate | |
| (70B) | 84-66-2 | diethyl phthalate | |
| (71B) | 131-11-3 | dimethyl phthalate | |
| (72B) | 56-55-3 | benzo(a)anthracene | |
| (73B) | 50-32-8 | benzo(a)pyrene | |
| (74B) | 205-99-2 | benzo(b)fluoranthene | |
| (75B) | 207-08-9 | benzo(k)fluoranthene | |
| (76B) | 218-01-9 | chrysene | |
| (77B) | 208-96-8 | acenaphthylene | |
| (78B) | 120-12-7 | anthracene | |
| (79B) | 191-24-2 | benzo(ghi)perylene | |
| (80B) | 86-73-7 | fluorene | |
| (81B) | 85-01-8 | phenanthrene | |
| (82B) | 53-70-3 | dibenzo(a,h)anthracene | |
| (83B) | 193-39-5 | indeno(1,2,3-cd)pyrene | |
| (84B) | 129-00-0 | pyrene | |
| | 62-53-3 | aniline | |
| | 100-51-6 | benzyl alcohol | |
| | 106-47-8 | 4-chloroaniline | |
| | 132-64-9 | dibenzofuran | |
| | 91-57-6 | 2-methylnaphthalene | |
| | 88-74-4 | 2-nitroaniline | |
| | 99-09-2 | 3-nitroaniline | |
| | 100-01-6 | 4-nitroaniline | ↓ |

1983

Environmental Protection Agency, CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313 703/557-2490

FRN 9372

| Sample Number |
|---|
| CHAMPION |

WASTE

5-31-85

## Organics Analysis Data Sheet
(Page 3)

### Pesticide/PCBs

Concentration: [✓ Low] Medium (Circle One)

Date Extracted/Prepared: 6-5-85

Date Analyzed: 6-10-85

[✓ Conc] Dil Factor: 200

| CAS Number | | [✓ ug/l] or ug/Kg (Circle One) |
|---|---|---|
| 319-84-6 | Alpha-BHC | < 2 |
| 319-85-7 | Beta-BHC | |
| 319-86-8 | Delta-BHC | |
| 58-89-9 | Gamma-BHC (Lindane) | |
| 76-44-8 | Heptachlor | |
| 309-00-2 | Aldrin | |
| 1024-57-3 | Heptachlor Epoxide | |
| 959-98-8 | Endosulfan I | |
| 60-57-1 | Dieldrin | |
| 72-55-9 | 4,4'-DDE | |
| 72-20-8 | Endrin | |
| 33213-65-9 | Endosulfan II | |
| 72-54-8 | 4,4'-DDD | |
| 7421-93-4 | Endrin Aldehyde | |
| 1031-07-8 | Endosulfan Sulfate | |
| 50-29-3 | 4,4'-DDT | |
| 72-43-5 | Methoxychlor | |
| 53494-70-5 | Endrin Ketone | |
| 57-74-9 | Chlordane | ↓ |
| 8001-35-2 | Toxaphene | N/A |
| 12674-11-2 | Aroclor-1016 | |
| 11104-28-2 | Aroclor-1221 | |
| 11141-16-5 | Aroclor-1232 | |
| 53469-21-9 | Aroclor-1242 | |
| 12672-29-6 | Aroclor-1248 | |
| 11097-69-1 | Aroclor-1254 | |
| 11096-82-5 | Aroclor-1260 | ↓ |

$V_i$ = Volume of extract injected (ul)

$V_s$ = Volume of water extracted (ml)

$W_s$ = Weight of sample extracted (g)

$V_t$ = Volume of total extract (ul)

$V_s$ ______ or $W_s$ ______ $V_t$ ______ $V_i$ ______

Form I 4/84

Form I. (continued).

FRN 1372

CHAMPION WASTE

5-31-85

# Organics Analysis Data Sheet
(Page 4)

## Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | [✓ RT] or Scan Number | Estimated Concentration ([✓ ug/l] or ug/kg) |
|---|---|---|---|---|
| 1. | 1-[2-(2-METHOXY-1-METHYLETHOXY)- | A/B/N | 16.58 | 547 |
| 2. | 1-METHYLETHOXY]-2-PROPANOL $C_{10}H_{22}O_4$ | | | |
| 3. | ISOMER OF #1 | | 16.93 | 190 |
| 4. | METHYLPENTADECANOIC ACID | | 26.78 | 116 |
| 5. | ANDROST-16-EN-3-ONE | | 26.98 | 62.6 |
| 6. | 1-EICOSENE $C_{20}H_{40}$ MW 280 | | 30.68 | 94.6 |
| 7. | ISOPIMARIC ACID MW 302 | | 31.22 | 155 |
| 8. | PIMARIC ACID MW 302 | | 31.65 | 375 |
| 9. | SIMILAR TO PIMARIC ACID MW302 | | 32.37 | 570 |
| 10. | DEHYDROABIETIC ACID MW 300 | | 32.83 | 905 |
| 11. | 15-HYDROXY-ANDROST-4-ENE-3 17-DIONE | | 33.28 | 240 |
| 12. | UNKNOWN ACID MW 340 | | 33.65 | 285 |
| 13. | 1-TETRACOSANOL $C_{24}H_{50}O$ | | 34.90 | 160 |
| 14. | ERGOST-5-EN-3-OL $C_{28}H_{48}O$ MW400 | | 41.88 | 194 |
| 15. | STIGMAST-5-EN-3-OL $C_{29}H_{50}O$ MW 414 | ↓ | 43.57 | 695 |
| 16. | | | | |
| 17. | | | | |
| 18. | | | | |
| 19. | | | | |
| 20. | | | | |
| 21. | | | | |
| 22. | | | | |
| 23. | | | | |
| 24. | | | | |
| 25. | | | | |
| 26. | | | | |
| 27. | | | | |
| 28. | | | | |
| 29. | | | | |
| 30. | | | | |

NATURAL ACIDS, KETONES + ALCOHOLS.

Page 1

ENVIRONMENTAL PROTECTION AGENCY
REGION VIII, DEN R, COLORADO

# LABORATORY SERVICES REQUEST

PROJECT NAME [illegible] PROJECT CODE ______ SAMPLES COLL. BY [illegible] DATE 5/31/85

SAMPLES RECEIVED AT LABORATORY BY [illegible] DATE [illegible] DATA REVIEWED BY ______

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| STATION CODE | | Samples taken, 5/31/85 | | | | | | | | | | | |
| SAMPLE COLL. TIME | | | | | | | | [illegible] | | [illegible] | | [illegible] | |
| STATION DESCRIPTION AND REMARKS [illegible] | | [illegible] Sta-11 | | [illegible] Sta-4 | | Clark Fork River at Missoula Sta-Airport | | [illegible] | | [illegible] (Clark Fork) | | [illegible] | |
| CODE | PARAMETER | | | | | | | | | | | | |
| [illegible] | [illegible] | ✓ | | | | | | ✓ | | | | | |
| [illegible] | | ✓ | | | | ✓ | | ✓ | | ✓ | | ✓ | |
| | Hg ug/l | | <5 | | <5 | | <5 | | <5 | | <5 | | <5 |
| | Al | | 3440 | | <30 | | 194 | | <30 | | 41 | | 4860 |
| | As | | 6 | | <5 | | <5 | | <5 | | <5 | | 8 |
| | Ba | | 171 | | 167 | | 68 | | 171 | | 68 | | <10 |
| | Be | | <10 | | <10 | | <10 | | <10 | | <10 | | <10 |
| | Cd | | <5 | | <5 | | <5 | | <5 | | <5 | | <5 |
| | Co | | <5 | | <5 | | <5 | | <5 | | <5 | | <5 |
| | Cr | | 13 | | <5 | | <5 | | <5 | | <5 | | 22 |
| | Cu | | <5 | | <5 | | 5 | | <5 | | <5 | | 7 |
| | Fe | | 434 | | <10 | | 230 | | <10 | | 90 | | 600 |
| | Mn | | 619 | | <5 | | 31 | | <5 | | 11 | | 770 |
| | Mo | | <10 | | <10 | | <10 | | <10 | | <10 | | <10 |
| | Ni | | <30 | | <30 | | <30 | | <30 | | <30 | | <30 |
| | Pb | | <30 | | <30 | | <30 | | <30 | | <30 | | <30 |

ANALYST INITIALS

results in mg/l unless otherwise indicated, heavy metals in ug/l, pH in units, turbidity in JTU, specific conductance in µ mhos/cm, as per STORET

☆ GPO · 1979-680 · 570

RBEPA-012
(Rev 11-82)

# D. FISHERIES STUDY AND BROWN TROUT BIOASSAY

Montana Department
of
Fish, Wildlife & Parks

# MIDDLE CLARK FORK RIVER FISHERY MONITORING STUDY:

## Evaluation of the Effects of Pulp and Paper Mill Effluents on the Fish Population

by

Montana Department of Fish, Wildlife and Parks
3201 Spurgin Road
Missoula, MT 59801
Phone: (406) 721-5808

Status Report
October 15, 1985

## Background

In July of 1983 Champion International Corporation applied to the Water Quality Bureau of the Montana Department of Health and Environmental Sciences for a modification of their waste water discharge permit for the Clark Fork River. If granted, the modified discharge permit would allow Champion to release pulp mill effluents into the Clark Fork River on a year-round basis. Under its existing permit the mill was limited to discharging pulp mill effluents only during spring high water. The permit modification was requested because Champion indicated its rapid infiltration system, a collection of gravel ponds to treat effluents, was becoming clogged to the extent that treated effluents would have to be released year-round.

After a preliminary environmental review, the Water Quality Bureau issued a temporary permit on April 10, 1984, which allowed Champion to release treated pulp mill effluents into the Clark Fork River on a year-round basis for two years. This led to an intense debate over existing and future impacts of pulp mill effluents on the river. Trout Unlimited and other environmental groups demanded an Environmental Impact Statement be completed before issuance of a permanent modified permit in two years. This was followed by numerous negotiations between Champion and the groups in an attempt to work out an agreement that would be acceptable to all sides and keep the issue out of court.

By the end of March 1984 a final agreement was reached that embodied the following points:

1. The State of Montana would prepare an Environmental Impact Statement at a cost of $200,000 before issuing a permanent modified discharge permit.

2. The Montana Department of Health and Environmental Sciences would monitor water quality from Turah to the Idaho line and attempt to identify all major sources of pollution and evaluate effects of pulp mill effluents on the water quality of the Clark Fork River. In conjunction Idaho agencies would test for impacts on the river in Idaho, including Lake Pend Oreille.

3. The Montana Department of Fish, Wildlife and Parks would undertake a two-year $100,000 study financed by Champion to evaluate effects of pulp mill effluents on the Clark Fork River fishery.

4. Champion agreed to sponsor an alternative methods study to consider technologies that would reduce or permanently eliminate discharges of pulp mill effluents into the river.

5. A twelve member technical advisory committee would meet on a regular basis to oversee the process. The committee included the broad based representation of Trout Unlimited, the Idaho Wildlife Federation, the Montana Environmental Information Center, the Green Monarch Coalition, Missoula/Mineral/Sanders County Commissioners Association, the Missoula County Health Department, the Water Quality Bureau, Fish, Wildlife and Parks, and Champion International Corporation.

Although the agreement did not represent a final solution, a thorough two-year study would begin to provide information needed to evaluate influences of the Champion Mill on the Clark Fork River.

## Scope of the Middle Clark Fork Fishery Study

The study area extends for about 120 miles from Milltown Dam to the confluence of the Flathead River. To evaluate the river's ability to safely assimilate additional quantities of pulp mill wastes, the current status of sport fish populations must be determined. Although fifteen species of fish are known to occur in the middle Clark Fork River, the bulk of the sport fishery is provided by rainbow trout along with a few cutthroat, brown and bull trout. The study is attempting to evaluate effects of pulp mill effluents on trout populations by assessing trout population characteristics in the river in areas upstream and downstream from the pulp mill effluent and by monitoring trout reproductive success in areas upstream and downstream from the effluent.

Trout population characteristics are being assessed by making population estimates. Factors which are being estimated include the number and biomass of trout per mile, species composition, condition factors, growth rates, age structure and mortality rates. Fish are being collected to make trout population estimates using boom suspended electrofishing apparatus. Much of the field work for this phase of the study is being accomplished at night because efficiency of the electrofishing system is significantly better at night than during day time. Trout population characteristics are being compared in study areas upstream and downstream from the pulp mill effluent to evaluate influences of the mill on the sport fishery.

Trout reproductive success is being monitored through a bioassay of trout egg and fry survival in the intergravel environment in study sites upstream and downstream from the pulp mill effluent. Egg and fry survival are being monitored for brown trout, a fall spawner. Egg and fry survival are being evaluated because the egg through emergent fry stage in the life cycle of trout may be relatively more vulnerable to possible influences of pulp mill pollutants than life stages after the trout fry have emerged from the spawning gravels.

Trout spawn in relatively shallow gravelly areas of the river with moderate current velocity. After a depression is dug in the spawning gravel by a female, eggs deposited in the depression by the female are fertilized by an accompanying male and covered over with four to eight inches of spawning gravel. Water quality factors of possible concern in the intergravel environment which could be influenced by pulp mill effluents include dissolved oxygen, pH, ammonia and fine sediments. Additional water quality parameters of concern may be identified during the course of investigation.

## Study Design Problems

There were several problems in designing this study to evaluate effects of pulp mill effluents on the sport fishery. First, the study was intended to document an impact from year round discharge of effluent from Champion's mill after the discharges had already begun. Second, there was very little baseline information on the condition of fish populations in areas downstream from the Champion discharge prior to the year-round discharge situation which now occurs. Third, the time frame for the study to assess impacts of the pulp mill was limited to two summer and one winter field seasons. This time frame was too short to provide an adequate assessment. Fourth, there are many other water quality problems in addition to pulp mill effluents which may affect the Clark Fork River fishery. Additional water quality factors which may be influencing the fishery include Missoula sewage treatment plant effluents, potentially toxic heavy metals originating from mine tailings in the upper Clark Fork drainage and fine sediments originating from various human related activities which could impair trout food production or trout reproductive success.

For these reasons, the scope of the study was broadened with additional funding and assistance being provided by the Department of Fish, Wildlife & Parks. A study was funded by the department to determine the relative importance of various tributaries as sources of recruitment for Clark Fork River trout populations. In addition, resident sport fishery values of the tributaries are being assessed and appropriate management recommendations will be made to maintain or improve fishery values of important tributaries.

To assist in identifying the potential influence of toxic metals on aquatic biota, DFWP is analyzing crayfish tissue samples. Potentially toxic heavy metals originating from mine tailings in the upper Clark Fork drainage are gradually diluted as the Clark Fork receives more good quality dilution water from downstream tributaries. However, monitoring has not been intensive enough, particularly from Milltown Dam downstream, to determine how often, if at all, metals criteria are exceeded. Crayfish were chosen as an indicator organism because their movements are confined to a relatively small area. Metals concentrations in crayfish exoskeletons may prove to be a good integrator of past history of exposure to metals.

The Department of Fish, Wildlife and Parks is also assessing the potential influence of pulp mill effluents on the taste of sport fish in the Clark Fork River. Taste tests will be conducted at an Oregon State University lab to evaluate the concentration at which pulp mill effluents adversely taint the taste of desirable sport fish.

The Department of Fish, Wildlife and Parks also believes that there is a need for a comprehensive evaluation of the Clark Fork River system which cannot be accomplished within the scope of ongoing studies. The comprehensive study should include quantification of instream flow requirements for sport fish in the main river as well as major tributaries, expand sampling to below the confluence of the Flathead River, assess seasonal and temporal distribution and movements of sport fish during both juvenile and adult life stages and identify interactions between fish populations and water quality relative to the influence of tributary streams.

Some of the above mentioned activities will be studied under continued redirection of department effort to the Clark Fork River. New funding will probably be required to complete portions of the comprehensive evaluation. Although the comprehensive evaluation cannot be completed in the short time frame required for the Champion Environmental Impact Statement, the data collected to that date will be made available and used.

## Outline
## Middle Clark Fork River Fishery Monitoring Study

I. Assessment of Influences of Pulp Mill Effluents on Trout Population Characteristics Including:

1. Number and Biomass (pounds) of Trout/Mile
2. Trout Species Composition
3. Condition Factors
4. Growth Rates
5. Age Structure
6. Mortality Rates

Method: Fish are being sampled with boom suspended electrofishing apparatus and estimates are being made using a mark/recapture technique.

II. Assessment of Influences of Pulp Mill Effluents on Trout Reproduction. Bioassay of brown trout egg and sac fry survival in the intergravel environment. Intergravel water quality parameters of possible concern which could be influenced by pulp mill waste products include dissolved oxygen, pH, ammonia and fine sediments. Bioassay sites include:

1. Council Grove Site - just upstream from Champion effluent
2. Champion site - immediately downstream from Champion effluent
3. Cyr site - downstream from the end of the pulp mill effluent mixing zone (about 25 miles downstream from the mill)

Method: Trout egg and fry survival are being monitored with fiberglass screen egg bags placed in the intergravel environment and with fry emergence traps placed over redds. Intergravel water quality samples are being collected using standpipes. Stream substrate samples are being collected using a McNeil core sampler.

III. Assessment of the Potential Influence of Toxic Heavy Metals on Aquatic Biota. Crayfish were chosen as an indicator organism because their movements are confined to a relatively small area. Toxic metals concentrations in crayfish exoskeletons may prove to be a good integrator of past history of exposure of an indicator organism to metals. Sampling locations for crayfish include below Milltown Dam, below the Missoula sewage outfall, below the Champion outfall, in the Bitterroot River (control), near Superior, below the Flathead River, below Thompson Falls Reservoir and below Noxon Reservoir.

IV. A more comprehensive evaluation of the Clark Fork River system which cannot be accomplished within the scope of ongoing studies is needed. The comprehensive study should include quantification of instream flow requirements for sport fish in the river as well as major tributaries, expand sampling to below the confluence of the Flathead River, assess seasonal and temporal distribution and movements of sport fish during both juvenile and adult life stages and identify interactions between fish populations and water quality relative to the influence of tributary streams.

## Preliminary Findings

1. Fifteen species representing six families of fish are found in the middle Clark Fork River between Milltown Dam and the confluence of the Flathead River (Table 1). Rainbow trout provide the bulk of the sport fishery along with a few brown, westslope cutthroat and bull trout.

2. Brown trout egg survival rates were lower at sites 2 and 3, Champion and Cyr, downstream from the pulp mill effluent than at site 1, Council Grove, the upstream control (Tables 2 and 10).

3. Lower egg survival rates occurred at Champion and Cyr even though measured gravel permeabilities were consistently higher at these sites compared to the control (Table 5). If other factors remain constant, higher permeability should enhance egg survival by increasing the rate of oxygen supply to incubating eggs.

4. Measurements of apparent velocity in the intergravel environment were very limited. However, apparent velocities monitored at each bioassay site from late February through early March indicated intergravel apparent velocity was highest at Cyr, lowest at Champion and intermediate at Council Grove (Table 4). Considerable difficulty was encountered in developing reliable techniques for measuring apparent velocity in the intergravel environment of the middle Clark Fork River. This accounts for the limited number of measurements made during the brown trout incubation period in 1984-85. Field experiments indicated standard standpipe methods for measuring apparent velocity were unsuitable for use in the Clark Fork because groundwater does not flow parallel to surface water. This violates a basic assumption for standpipe methods that groundwater does flow parallel to surface water. To replace standpipes, a variety of sizes and types of seepage meters were constructed and tested to measure apparent velocity. The limited findings in Table 4 are based on measurements of apparent velocity from these seepage meters.

5. If other factors remain constant, higher apparent velocity should enhance egg survival by increasing the rate of oxygen supply to incubating eggs.

6. Dissolved oxygen concentrations in the intergravel environment ranged to considerably lower levels at Champion and Cyr than at Council Grove (Table 7). Low dissolved oxygen concentrations in the intergravel environment can reduce trout egg survival rates during the incubation period.

7. Substrate composition was most favorable for egg survival at the Champion bioassay site (Table 14).

8. Dissolved oxygen concentration, permeability, apparent velocity and substrate composition interact to influence trout egg survival in the intergravel environment.

9. Preliminary observations suggest concentrations of cadmium and zinc in the intergravel environment are not high enough to adversely affect trout egg survival rates (Table 8). Additional monitoring of copper and iron concentrations in the intergravel environment is needed to determine whether levels are high enough to influence trout egg survival rates (Glenn Phillips, Montana Department of Fish, Wildlife and Parks and Gary Ingman, Montana Department of Health and Environmental Sciences, personal communication).

10. Preliminary observations indicate concentrations of ammonia in the intergravel environment are not high enough to adversely affect trout egg survival rates (Table 8) (Glenn Phillips, Montana Department of Fish, Wildlife and Parks, personal communication).

11. Water depth and velocity remained within acceptable criteria for brown trout egg survival during the incubation period (Table 3 and Figure 1).

12. Embryo development was slower at the Champion and Cyr sites than at Council Grove (Table 10). By mid-March, 1985, the eyed egg bioassay was developed to 97.8 percent sac fry at Council Grove compared to 53.7 and 49.1 percent sac fry at Champion and Cyr, respectively.

13. Elevated concentrations of sodium and chloride ions in water samples collected from the intergravel environment at Champion and Cyr suggest Champion effluent affects intergravel water quality for a distance of at least 25.6 miles downstream from the effluent discharge (Table 9).

14. Limited electrofishing surveys indicated young-of-the-year trout were relatively more abundant in the Milltown and Superior study sections than in the Missoula and Huson sections during late summer of 1985 (Table 11).

15. Preliminary estimates of catchable rainbow trout in four study sections of the Clark Fork River are shown in Table 12. Rainbow trout provide the bulk of the sport fishery in the middle Clark Fork River. While the Clark Fork roughly doubles in size between the Milltown and Superior study sections, preliminary estimates indicate trout populations do not increase at this same magnitude. Locations of the trout population estimate study sections are shown in Table 13.

## Summary

Fishery studies conducted to date on the middle Clark Fork River suggest Champion effluent affects intergravel water quality for a distance of at least 25.6 miles downstream from the discharge. Findings from a field bioassay indicated brown trout egg survival rates were lower at sites immediately downstream and 25.6 miles downstream from the pulp mill effluent than at an upstream control. Brown trout embryo development was also significantly slower at sites downstream from the pulp mill effluent than at the upstream control.

Intergravel water quality will be monitored by the Department of Fish, Wildlife and Parks (DFWP) at eight study sites on the Clark Fork River during the brown/rainbow trout incubation period in 1985-86. In addition to the Council Grove, Champion and Cyr bioassay sites established in the fall of 1984, intergravel water quality will be monitored at sites near Milltown Dam, in the main channel of the Clark Fork River near Council Grove, near the Erskine Fishing Access (several miles downstream of the Champion effluent discharge and within the mixing zone), near Huson (below the Champion mixing zone) and near Superior (also below the Champion mixing zone). This will provide a total of three monitoring sites upstream from the pulp mill effluent discharge and five downstream from the discharge.

Intergravel water quality parameters which will be monitored during the brown/rainbow trout incubation period in 1985-86 include total recoverable concentrations of iron and copper, total hardness, total alkalinity, pH, water temperature, dissolved oxygen, conductivity, total suspended solids, volatile suspended solids and concentrations of chloride, sodium, calcium and magnesium. The intergravel studies are being conducted to continue to evaluate environmental factors potentially affecting trout egg survival rates in the Clark Fork River and to more accurately assess potential direct or indirect affects of Champion effluent discharge on trout reproductive success.

Even though the Clark Fork River approximately doubles in size between the Milltown and Superior study sections, preliminary estimates made during 1984-85 indicate trout populations do not increase at the same magnitude. DFWP will estimate trout populations in the Milltown, Missoula, Huson and Superior sections in 1986 to monitor population changes compared to earlier baseline estimates. Environmental factors potentially influencing trout population characteristics in the four study sections will also be assessed. Factors such as stream gradient, channel development, water temperature and water chemistry will be measured to aid in evaluating differences in population characteristics between study sections and to continue to more accurately evaluate whether trout population characteristics are affected by Champion effluent discharge. The Milltown and Missoula sections are located upstream from the Champion effluent while the Huson and Superior sections are located downstream from the Champion effluent and downstream from the effluent mixing zone.

DFWP will conduct electrofishing surveys in 1985-86 to document species of nongame and forage fish present and their relative abundance in the Milltown, Missoula, Huson and Superior study sections. Forage fish are important constituents in the diet of trout, particularly brown and bull trout. The surveys will aid in beginning to identify potential differences in trout food supply between the sections and in evaluating whether the trout food supply is affected by Champion effluent discharge.

Potential impacts of year round discharge of pulp mill effluents on trout populations and the sport fishery of the middle Clark Fork River represent a legitimate public concern. Additional time is needed to adequately assess potential impacts of year round discharge on trout reproductive success, trout population characteristics, trout food supply and sport fishing success rates. A minimum of five years will be required for a reliable assessment of these impacts.

Table 1. Fish species found in the Clark Fork River in Montana between Milltown Dam and the confluence of the Flathead River.

| | |
|---|---|
| SALMONIDAE (Trout Family) | |
| *Prosopium williamsoni* - Mountain whitefish | A1/ |
| *Salmo clarki lewisi* - Westslope cutthroat trout | R* |
| *Salmo gairdneri* - Rainbow trout | C |
| *Salmo trutta* - Brown trout | R* |
| *Salvelinus fontinalis* - Brook trout | R* |
| *Salvelinus confluentus* - Bull trout | R |
| ESOCIDAE (Pike Family) | |
| *Esox lucius* - Northern pike | R |
| CYPRINIDAE (Minnow Family) | |
| *Mylocheilus caurinus* - Peamouth | R |
| *Ptychocheilus oregonensis* - Squawfish | A |
| *Rhinichthys cataractae* - Longnose dace | C |
| *Richardsonius balteatus* - Redside shiner | A |
| CATOSTOMIDAE (Sucker Family) | |
| *Catostomus catostomus* - Longnose sucker | R |
| *Catostomus macrocheilus* - Largescale sucker | A |
| CENTRARCHIDAE (Sunfish Family) | |
| *Micropterus salmoides* - Largemouth bass | R |
| COTTIDAE (Sculpin Family) | |
| *Cottus cognatus* - Slimy sculpin | C |

1/ Relative Abundance - A = Abundant, C = Common, R = Rare.
* Common in some tributaries of the Clark Fork in the study area.

Table 2. Study site names, river mileage locations and legal descriptions of brown trout bioassay sites.

| Site No. | Site Name | Approximate River Mile | Legal Description |
|---|---|---|---|
| 1 | Council Grove | 343.5 | T13N, R20W, S06 DCC |
| 2 | Champion | 338.6 | T14N, R21W, S14 BBB |
| 3 | Cyr | 313.0 | T14N, R23W, S06 BCC |

Table 3. Physical habitat parameters of brown trout egg bioassay sites in the Clark Fork River during the incubation period. Standard deviations are in parentheses.

| Date | Site | Egg Type | Depth (ft) |  | Mean Velocity (ft/sec) |  | Point Velocity (ft/sec) |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | N | $\bar{x}$ | N | $\bar{x}$ | N | $\bar{x}$ |
| 11/15-16/84 | 1 | Green | 6 | 0.94(±0.19) | 6 | 2.09(±0.60) | 6 | 1.09(±0.41) |
| " | 2 | Green | 6 | 0.96(±0.05) | 6 | 2.41(±0.11) | 6 | 1.08(±0.42) |
| " | 3 | Green | 6 | 1.00(±0.17) | 6 | 1.98(±0.51) | 6 | 1.17(±0.44) |
| 12/8/84 | 1 | Green | 1 | 0.7 | 1 | 1.15 | 1 | 0.45 |
| " | 2 | Green | 1 | 0.55 | 1 | 0.1 | 1 | 0.0 |
| " | 3 | Green | 1 | 0.75 | 1 | 0.75 | 1 | 0.25 |
| 1/15-17/85 | 1 | Green | 6 | 0.77(±0.30) | 6 | 1.22(±0.64) | 6 | 0.50(±0.40) |
| " | 2 | Green | 6 | 0.47(±0.13) | 6 | 0.50(±0.08) | 6 | 0.23(±0.11) |
| " | 3 | Green | 6 | 0.28(±0.14) | 6 | 0.09(±0.15) | - |  |
| " | 1 | Eyed | 5 | 1.29(±0.12) | 5 | 2.28(±0.37) | 5 | 0.78(±0.39) |
| " | 2 | Eyed | 5 | 1.24(±0.29) | 5 | 1.75(±0.37) | 5 | 0.63(±0.24) |
| " | 3 | Eyed | 4 | 0.66(±0.14) | 4 | 2.15(±0.27) | - |  |
| 1/22-24/85 | 1 | Green | 6 | 0.68(±0.30) | 6 | 1.17(±0.90) | 6 | 0.54(±0.46) |
| " | 2 | Green | 6 | 0.37(±0.10) | 6 | 0.25(±0.08) | 6 | 0.06(±0.08) |
| " | 3 | Green | 6 | 0.99(±0.27) | 6 | 1.88(±0.30) | 6 | 0.76(±0.25) |
| " | 1 | Eyed | 5 | 1.17(±0.06) | 5 | 2.29(±0.35) | 5 | 1.20(±0.39) |
| " | 2 | Eyed | 5 | 1.11(±0.19) | 5 | 1.56(±0.24) | 5 | 0.70(±0.27) |
| " | 3 | Eyed | 4 | 1.38(±0.38) | 4 | 3.09(±0.71) | 4 | 1.38(±0.31) |
| 2/22,25/85 | 1 | Green | 6 | 0.72(±0.29) | 6 | 1.14(±0.76) | 6 | 0.37(±0.32) |
| " | 2 | Green | 6 | 0.41(±0.13) | 6 | 0.49(±0.16) | 6 | 0.28(±0.20) |
| " | 3 | Green | 6 | 0.95(±0.25) | 6 | 1.73(±0.30) | 6 | 0.73(±0.41) |
| " | 1 | Eyed | 5 | 1.22(±0.10) | 5 | 2.42(±0.29) | 5 | 0.84(±0.18) |
| " | 2 | Eyed | 5 | 1.21(±0.29) | 5 | 1.77(±0.23) | 5 | 0.78(±0.28) |
| " | 3 | Eyed | 4 | 1.13(±0.05) | 4 | 3.08(±0.71) | 4 | 0.83(±0.38) |
| 3/14-15/85 | 1 | Green | 6 | 0.72(±0.26) | 6 | 1.49(±0.66) | 6 | 0.75(±0.30) |
| " | 2 | Green | 6 | 0.55(±0.09) | 6 | 0.79(±0.23) | 6 | 0.32(±0.20) |
| " | 3 | Green | 6 | 0.90(±0.25) | 6 | 1.79(±0.29) | 6 | 0.73(±0.26) |
| " | 1 | Eyed | 5 | 1.27(±0.10) | 5 | 2.66(±0.30) | 5 | 1.09(±0.33) |
| " | 2 | Eyed | 5 | 1.42(±0.31) | 5 | 1.78(±0.26) | 5 | 0.69(±0.15) |
| " | 3 | Eyed | 4 | 1.08(±0.10) | 4 | 2.96(±0.57) | 4 | 1.08(±0.10) |
| 3/27,29 & 4/3/85 | 1 | Green | 6 | 0.73(±0.30) | 6 | 1.83(±0.82) | 6 | 1.00(±0.32) |
|  | 2 | Green | 6 | 0.70(±0.08) | 6 | 1.38(±0.12) | 6 | 0.63(±0.15) |
| " | 3 | Green | 6 | 1.62(±0.19) | 6 | 2.44(±0.19) | 6 | 0.90(±0.33) |
| " | 1 | Eyed | 5 | 1.29(±0.18) | 5 | 2.47(±0.29) | 5 | 1.42(±0.15) |
| " | 2 | Eyed | 5 | 1.56(±0.30) | 5 | 1.94(±0.19) | 5 | 0.74(±0.20) |
| " | 3 | Eyed | 4 | 2.11(±0.10) | 4 | 2.74(±0.33) | 4 | 0.75(±0.27) |

Table 4. Groundwater flow into the Clark Fork River measured by seepage meters at brown trout egg bioassay sites. Standard deviations are in parentheses.

| Site | Date | No. of measurements | Apparent velocity ml/m$^2$. min | Apparent velocity cm/hr |
|---|---|---|---|---|
| 2 | 12/19/84-1/4/85 | 3 | 0.70 (±0.69) | 0.25 (±0.25) |
| 1 | 2/22-3/5/85 | 2 | 0.34 (±0.15) | 0.12 (±0.06) |
| 2 | 2/21-3/5/85 | 2 | 0.14 (±0.04) | 0.05 (±0.01) |
| 3 | 2/25-3/5/85 | 2 | 0.80 (±0.04) | 0.29 (±0.01) |
| 2 | 3/6-3/22/85 | 2 | 1.02 (±0.37) | 0.37 (±0.13) |
| 2 | 3/27-4/2/85 | 3 | - | 3.71 (±2.80) |

Table 5. Permeabilities at 10 C from the brown trout bioassay sites in the Clark Fork River. Standard deviations are in parentheses.

| Date | Site | Egg Type | Number (N) | Permeability $K_{10}$ (cm/min) | Permeability $K_{10}$ (cm/hr) |
|---|---|---|---|---|---|
| 11/19-20/84 | 1 | Green | 6 | 0.9 (±0.6) | 54 (±36) |
| " | 2 | Green | 6 | 5.0 (±2.4) | 300 (±144) |
| " | 3 | Green | 6 | 2.6 (±2.6) | 156 (±156) |
| 1/22-25/85 | 1 | Green | 6 | 3.4 (±0.8) | 204 (±48) |
| " | 2 | Green | 6 | 7.5 (±5.2) | 450 (±312) |
| " | 3 | Green | 6 | 10.1 (±1.4) | 606 (±84) |
| " | 1 | Eyed | 6 | 3.9 (±1.9) | 234 (±114) |
| " | 2 | Eyed | 6 | 8.3 (±4.0) | 498 (±240) |
| " | 3 | Eyed | 6 | 24.6 (±9.2) | 1476 (±552) |
| 3/28-29 & 4/3/85 | 1 | Green | 6 | 3.0 (±1.9) | 180 (±114) |
|  | 2 | Green | 6 | 6.0 (±4.4) | 360 (±264) |
| " | 3 | Green | 6 | 5.3 (±2.8) | 318 (±168) |
| " | 1 | Eyed | 6 | 4.4 (±2.3) | 264 (±138) |
| " | 2 | Eyed | 6 | 16.8 (±11.7) | 1008 (±702) |
| " | 3 | Eyed | 1 | 24.4 | 1464 |

Table 6. Dissolved oxygen concentrations from brown trout egg bioassay sites in the Clark Fork River. Standard deviations are in parentheses.

| Site | Date | Sample Source | Egg Type | N | Dissolved Oxygen (mg/l) |
|---|---|---|---|---|---|
| 1 | 11/15/84 | Surface | - | 1 | 11.4 |
| 1 | " | Gravel | Green | 4 | 10.9 (±0.3) |
| 2 | " | Surface | - | 1 | 13.5 |
| 2 | " | Gravel | Green | 3 | 4.9 (±3.0) |
| 3 | 11/16/84 | Surface | - | 1 | 13.9 |
| 3 | " | Gravel | Green | 4 | 12.3 (±0.5) |
| 2 | 12/13/84 | Surface | - | 1 | 13.0 |
| 2 | " | Gravel | Green | 1 | 3.3 |
| 2 | " | Gravel | Eyed | 1 | 8.5 |
| 1 | 12/17/84 | Surface | - | 1 | 11.4 |
| 1 | " | Gravel | Green | 3 | 10.2 (±0.3) |
| 2 | " | Surface | - | 1 | 14.1 |
| 2 | " | Gravel | Green | 3 | 10.3 (±2.1) |
| 3 | 12/14/84 | Surface | - | 1 | 13.6 |
| 3 | " | Gravel | Green | 3 | 13.1 (±0.3) |
| 1 | 1/30/85 | Surface | - | 1 | 12.3 |
| 1 | " | Gravel | Green & Eyed | 5 | 10.6 (±1.1) |
| 2 | 1/29/85 | Surface | - | 2 | 13.7 (±0.1) |
| 2 | " | Gravel | Green | 2 | 5.8 (±1.5) |
| 2 | " | Gravel | Eyed | 2 | 11.7 (±1.1) |
| 3 | " | Surface | - | 1 | 13.0 |
| 3 | " | Gravel | Green | 2 | 10.2 (±0.5) |
| 3 | " | Gravel | Eyed | 3 | 10.7 (±1.2) |
| 1 | 2/28/85 | Surface | - | - | - |
| 1 | " | Gravel | Green & Eyed | 5 | 8.7 (±0.7) |
| 2 | " | Surface | - | 2 | 12.7 (±0.1) |
| 2 | " | Gravel | Green | 3 | 5.2 (±2.6) |
| 2 | " | Gravel | Eyed | 3 | 9.5 (±2.0) |
| 3 | 3/1/85 | Surface | - | 1 | 11.9 |
| 3 | " | Gravel | Green | 5 | 8.2 (±1.6) |
| 3 | " | Gravel | Eyed | 4 | 6.0 (±1.3) |
| 1 | 4/1/85 | Surface | - | 1 | 12.6 |
| 1 | " | Gravel | Green & Eyed | 5 | 8.7 (±1.5) |
| 2 | " | Surface | - | 1 | 11.7 |
| 2 | " | Gravel | Green | 3 | 0.7 (±0.4) |
| 2 | " | Gravel | Eyed | 3 | 8.1 (±3.9) |
| 3 | " | Surface | - | 1 | 11.4 |
| 3 | " | Gravel | Green | 3 | 8.1 (±2.2) |
| 3 | " | Gravel | Eyed | 3 | 7.4 (±1.2) |

Table 7. Overall mean dissolved oxygen concentrations from brown trout egg bioassay sites in the Clark Fork River. Standard deviations are in parentheses.

| Site | Sample source | Egg type | N | Mean Dissolved Oxygen (mg/l) | Dissolved Oxygen Range (mg/l) |
|---|---|---|---|---|---|
| 1 | Surface | - | 4 | 11.9 (± 0.6) | 11.4 - 12.6 |
| | Gravel | Green & eyed | 21 | 9.6 (± 1.2) | 7.2 - 12.3 |
| 2 | Surface | - | 8 | 13.1 (± 0.8) | 11.7 - 14.1 |
| | Gravel | Green | 15 | 5.2 (± 3.6) | 0.4 - 12.2 |
| | Gravel | Eyed | 9 | 9.4 (± 2.6) | 3.9 - 12.5 |
| 3 | Surface | - | 5 | 12.8 (± 1.1) | 11.4 - 13.85 |
| | Gravel | Green | 17 | 10.2 (± 2.5) | 5.7 - 13.5 |
| | Gravel | Eyed | 10 | 7.8 (± 2.3) | 4.2 - 11.7 |

Table 8. Intragravel water quality at brown trout egg bioassay sites in the Clark Fork River. Standard deviations are in parentheses.

| | Site 1 Council Grove | | | | Site 2 Champion side channel | | | |
|---|---|---|---|---|---|---|---|---|
| | Intragravel | | Surface | | Intragravel | | Surface | |
| Parameter | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| T.S.S. (mg/l) | 16.0(±10.8) | 4.8-37.8 | 2.0(±1.0) | 1.1-3.0 | 74.2(±108.8) | 0.8-332.3 | 1.8(±0.1) | 1.7-1.9 |
| V.S.S. (mg/l) | 3.1(± 2.1) | 1.2-8.1 | 1.2(±0.1) | 1.1-1.3 | 18.4(±16.8) | 6.1-52.8 | 1.4(±0.0) | N=2 |
| Total Alkalinity | | | | | | | | |
| (mg/l CaCO$_3$) | 109.3(±15.2) | 68.0-121.0 | 114.0(±3.3) | 109.0-118.0 | 344.8(±175.6) | 133.0-686.0 | 115.2(±3.9) | 109.0-119.0 |
| Total Hardness | | | | | | | | |
| (mg/l CaCO$_3$) | 126.0(±35.1) | 44.0-166.0 | 133.7(±1.5) | 132.0-135.0 | 181.9(±38.4) | 131.0-253.0 | 129.3(±3.2) | 127.0-133.0 |
| Total Recoverable | | | | | | | | |
| Cu (mg/l) | < 0.01 | N=5 | < 0.01 | N=2 | 0.02(±0.01) | 0.01-0.03 | < 0.01 | N=2 |
| Fe (mg/l) | 0.20(±0.09) | 0.14-0.35 | 0.05(±0.0) | N=2 | 0.98(±0.92) | 0.16-2.44 | 0.07(±0.0) | N=2 |
| Cd (mg/l) | < 0.005 | N=5 | < 0.005 | N=2 | 0.005(±0.001) | 0.002-0.005 | < 0.005 | N=2 |
| Zn (mg/l) | 0.03(±0.01) | 0.01-0.04 | 0.006(±0.001) | 0.005-0.006 | 0.035(±0.035) | 0.005-0.10 | < 0.005 | N=2 |
| pH | 8.06(±0.12) | 7.81-8.20 | 8.31(±0.18) | 8.14-8.60 | 7.87(±0.15) | 7.70-8.20 | 8.23(±0.18) | 7.94-8.39 |
| NH$_3$ as N (mg/l) | 0.013(±0.005) | 0.01-0.02 | 0.01(±0.00) | N=3 | 0.50(±0.31) | 0.02-0.91 | 0.03(±0.03) | 0.01-0.06 |
| NO$_3$ as N (mg/l) | 0.232(±0.127) | 0.142-0.321 | 0.101(±0.022) | 0.085-0.116 | 0.179(±0.069) | 0.130-0.228 | 0.107(±0.049) | 0.072-0.14 |
| PO$_4$ as P (mg/l) | 0.028(±0.009) | 0.021-0.034 | 0.027(±0.000) | N=2 | 0.035(±0.010) | 0.028-0.042 | 0.036(±0.009) | 0.029-0.04 |
| T.D.S. (mg/l) | 211.4(±4.5) | 208.2-214.5 | 214.7(±1.8) | 213.4-215.9 | 213.7(±8.0) | 208.0-219.3 | 225.6(±5.2) | 221.9-229.2 |

Table 8. (Cont.)

| Parameter | Site 2<br>Champion main channel | | | | Site 3<br>Cyr | | | |
|---|---|---|---|---|---|---|---|---|
| | Intragravel | | Surface | | Intragravel | | Surface | |
| | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| T.S.S. (mg/l) | 60.1(±18.2) | 47.2-73.0 | 2.7 | N=1 | 12.4(±6.8) | 1.9-20.1 | 2.7(±1.2) | 1.8-4.1 |
| V.S.S. (mg/l) | 11.2(±1.6) | 10.1-12.3 | 1.6 | N=1 | 2.6(±1.4) | 1.0-5.7 | 1.6(±0.3) | 1.2-1.8 |
| Total Alkalinity (mg/l $CaCO_3$) | 115.3(±2.75) | 112.0-118.0 | 115.3(±4.7) | 110.0-119.0 | 105.3(±13.5) | 76.0-118.0 | 112.2(±4.0) | 107.0-118. |
| Total Hardness (mg/l $CaCO_3$) | 130.0(±4.2) | 127.0-133.0 | 131.0 | N=1 | 116.0(±18.7) | 73.0-134.0 | 129.0(±8.5) | 123.0-135. |
| Total Recoverable | | | | | | | | |
| Cu (mg/l) | <0.01 | N=1 | <0.01 | N=1 | <0.01 | N=5 | <0.01 | N=2 |
| Fe (mg/l) | 0.30 | N=1 | 0.07 | N=1 | 0.11(±0.07) | 0.04-0.22 | 0.045(±0.007) | 0.04-0.0 |
| Cd (mg/l) | <0.005 | N=1 | 0.005 | N=1 | <0.005 | N=5 | <0.005 | N=2 |
| Zn (mg/l) | 0.03 | N=1 | 0.005 | N=1 | 0.016(±0.015) | 0.005-0.04 | 0.0065(±0.002) | 0.005-0.00 |
| pH | 8.06(±0.19) | 7.90-8.33 | 8.40(±0.10) | 8.30-8.50 | 8.18(±0.10) | 8.04-8.32 | 8.35(±0.10) | 8.25-8.5 |
| $NH_3$ as N (mg/l) | 0.03(±0.02) | 0.02-0.04 | 0.01 | N=1 | 0.01(±0.004) | 0.01-0.02 | 0.01(±0.0) | N=3 |
| $NO_3$ as N (mg/l) | 0.21(±0.04) | 0.179-0.237 | 0.108(±0.064) | 0.063-0.153 | 0.179(±0.069) | 0.130-0.228 | 0.110(±0.061) | 0.067-0.15 |
| $PO_4$ as P (mg/l) | 0.08(±0.04) | 0.05-0.10 | 0.035(±0.008) | 0.029-0.040 | 0.035(±0.010) | 0.028-0.042 | 0.029(±0.004) | 0.026-0.03 |
| T.D.S. (mg/l) | 226.8(±2.47) | 225.0-228.5 | 224.3(±1.1) | 223.5-225.1 | 213.7(±8.0) | 208.0-219.3 | 215.3(±3.2) | 213.0-217. |

Table 9. Major cation/anion concentrations from brown trout egg bioassay sites in the Clark Fork River.

| Date | Site | Sample Source | Mean concentration (mg/l) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $SO_4^{-2}$ | $Cl^-$ | $Na^+$ | $K^+$ | $Ca^{+2}$ | $Mg^{+2}$ |
| 3/5/85 | 1 | Gravel | 21.2 | 3.1 | 7.5 | 2.3 | 30.0 | 11.1 |
| | | Surface | 21.4 | 3.1 | 7.3 | 2.1 | 30.6 | 11.0 |
| | 2 | Gravel-side channel | 142.0 | 43.1 | 144.0 | 4.5 | 34.9 | 17.7 |
| | | Surface-side channel | 24.0 | 5.0 | 13.6 | 2.2 | 30.0 | 11.0 |
| | | Gravel-main river | 21.6 | 4.9 | 12.6 | 2.3 | 30.3 | 9.7 |
| | | Surface-main river | 21.6 | 4.9 | 12.6 | 2.3 | 30.3 | 9.7 |
| | 3 | Gravel | 24.5 | 4.1 | 10.2 | 2.5 | 29.7 | 10.9 |
| | | Surface | 21.0 | 4.1 | 10.1 | 2.4 | 30.0 | 10.8 |
| 4/2/85 | 1 | Gravel | 22.7 | 2.8 | 6.6 | 2.0 | 30.9 | 10.2 |
| | | Surface | 25.9 | 2.7 | 7.1 | 1.8 | 31.8 | 10.4 |
| | 2 | Gravel-side channel | 404.0 | 123.0 | 388.0 | 8.5 | 68.2 | 28.5 |
| | | Surface-side channel | 31.0 | 4.1 | 11.4 | 1.9 | 30.8 | 10.0 |
| | | Gravel-main river | 30.2 | 4.1 | 11.4 | 2.0 | 31.8 | 10.5 |
| | | Surface-main river | 31.2 | 4.0 | 11.4 | 1.8 | 31.2 | 10.0 |
| | 3 | Gravel | 21.9 | 3.6 | 9.1 | 2.1 | 29.8 | 10.1 |
| | | Surface | 27.0 | 3.5 | 9.3 | 1.8 | 30.6 | 9.6 |

Table 10. Egg survival from three bioassay sites in the Clark Fork River.

| Date | Site | Egg Type | Percent Survival | Eggs Live, | Dead | Stage of Development (Live Eggs) |
|---|---|---|---|---|---|---|
| 11/19-20/84 | 1 | Green | 98.1 | 159 | 3 | 100% Green |
| " | 2 | Green | 98.8 | 163 | 2 | 100% Green |
| " | 3 | Green | 95.6 | 151 | 7 | 100% Green |
| 12/8/84 | 1 | Green | 95.0 | 151 | 8 | 100% Green |
| " | 2 | Green | 92.0 | 149 | 13 | 100% Green |
| " | 3 | Green | 92.5 | 149 | 12 | 100% Green |
| 1/22-24/85 | 1 | Green | 89.0 | 145 | 18 | 100% Green |
| " | 2 | Green | 78.8 | 130 | 35 | 100% Green |
| " | 3 | Green | 94.3 | 150 | 9 | 100% Green |
| " | 1 | Eyed | 91.4 | 148 | 14 | 99.3% Eyed,0.7% Sac Fry |
| " | 2 | Eyed | 92.6 | 150 | 12 | 100% Eyed |
| " | 3 | Eyed | 92.0 | 150 | 13 | 100% Eyed |
| 2/21,22&25/85 | 1 | Green | 92.0 | 149 | 13 | 2.0% Green,96.6% Eyed,1.3% Sac Fry |
| " | 2 | Green | 0.0* | 0 | 162 | - |
| " | 3 | Green | 0.0* | 0 | 158 | - |
| " | 1 | Eyed | 91.5 | 150 | 14 | 95.3% Eyed,4.7% Sac Fry |
| " | 2 | Eyed | 70.8 | 114 | 47 | 100% Eyed |
| " | 3 | Eyed | 83.9 | 135 | 26 | 98.5% Eyed,1.5% Sac Fry |
| 3/14-15/85 | 1 | Green | 86.8 | 46 | 7 | 4.3% Green,91.3% Eyed,4.3% Sac Fry |
| " | 2 | Green | 0.0 | 0 | 164 | - |
| " | 3 | Green | 0.0 | 0 | 157 | - |
| " | 1 | Eyed | 85.3 | 139 | 24 | 2.2% Eyed,97.8% Sac Fry |
| " | 2 | Eyed | 66.3 | 108 | 55 | 46.3% Eyed,53.7% Sac Fry |
| " | 3 | Eyed | 65.8 | 106 | 55 | 50.9% Eyed,49.1% Sac Fry |
| 3/27,29 & 4/2/85 | 1 | Green | 91.7 | 143 | 13 | 2.1% Green,94.4% Eyed,3.5% Sac Fry |
|  | 2 | Green | 0.0 | 0 | 162 | - |
|  | 3 | Green | 0.0 | 0 | 161 | - |
|  | 1 | Eyed | 83.2 | 134 | 27 | 100% Sac Fry |
|  | 2 | Eyed | 72.4 | 110 | 42 | 100% Sac Fry |
|  | 3 | Eyed | 48.6 | 52 | 55 | 100% Sac Fry |

* Green egg bioassay terminated due to egg freeze-up.

Table 11. Average size and relative abundance of young-of-the-year trout sampled by electrofishing in four study sections of the Clark Fork River during late summer 1985.

| Study Section | Date | Trout Species | Average Length (mm) | Juvenile Trout Electrofished/Hour |
|---|---|---|---|---|
| Milltown | 8/26/85 | Rainbow | 57 | 7.1 |
| | | Brown | 90 | 10.7 |
| Missoula (side channel) | 8/28/85 | Rainbow | 76 | 1.7 |
| | | Brown | 94 | 10.0 |
| Missoula (main river) | 8/28/85 | Rainbow | 63 | 1.4 |
| | | Brown | - | 0.0 |
| Huson | 8/30 &<br>9/4/85 | Rainbow | 60 | 3.6 |
| | | Brown | 77 | 0.3 |
| Superior | 9/5/85 | Rainbow | 58 | 14.6 |
| | | Brown | 81 | 1.1 |

Table 12. Preliminary trout population estimates in four study sections of the Clark Fork River.

| Study Section | Date of Estimate | Fish Species | Section Length(mi) | Catchable[1/] Trout/Section | Catchable[1/] Trout/Mile |
|---|---|---|---|---|---|
| Missoula | Sept. 1984 | Rainbow | 8.6 | 1506 | 175 |
| Missoula | June 1985 | Rainbow | 8.6 | 1804 | 210 |
| Milltown | June 1985 | Rainbow | 3.6 | 1035 | 288 |
| Superior | July 1985 | Rainbow | 6.3 | 1382 | 219 |
| Huson | Sept. 1985 | Rainbow | 4.5 | 1749 | 389 |

[1/] Catchable trout 7-inches total length and larger

Table 13. Location, length and river mile index boundaries of fish population study sections on the Clark Fork River.

| Section Name | Description of Location | Section Length (mi) | River Mile Index Boundaries |
|---|---|---|---|
| Milltown | Milltown Dam to 2.8 miles upstream from confluence of Rattlesnake Cr. | 3.4 | 364.4 to 361.0 |
| Missoula | Confluence of Bitterroot R. to 0.5 mile upstream from Harper Bridge | 8.6 | 350.5 to 341.9 |
| Huson | Confluence of Sixmile Cr. to 4.0 miles upstream from confluence of Petty Cr. | 4.5 | 328.2 to 323.7 |
| Superior | Confluence of Cedar Cr. to confluence of Dry Cr. | 6.3 | 286.6 to 280.3 |

Table 14. Fine substrate composition at green and eyed brown trout egg bioassay sites on the Clark Fork River.

| Egg Type | Bioassay Site | Percentage of materials passing through 0.84-mm sieve (± standard deviation)* |
|---|---|---|
| Green | 1 | 23.20% (± 1.61) |
| | 2 | 10.59% (± 3.39) |
| | 3 | 19.07% (± 2.93) |
| Eyed | 1 | 16.06% (± 4.21) |
| | 2 | 12.68% (± 0.85) |
| | 3 | 23.26% (±11.04) |

* Spawning success may be impaired where bottom materials contain more than 15 to 20 percent of materials passing through an 0.84-mm sieve (McNeil, W. J. and W. H. Ahnell, 1964. Success of pink salmon spawning relative to size of spawning bed materials. USDI, Fish and Wildlife Service. Special Scientific Report: Fisheries No. 469).

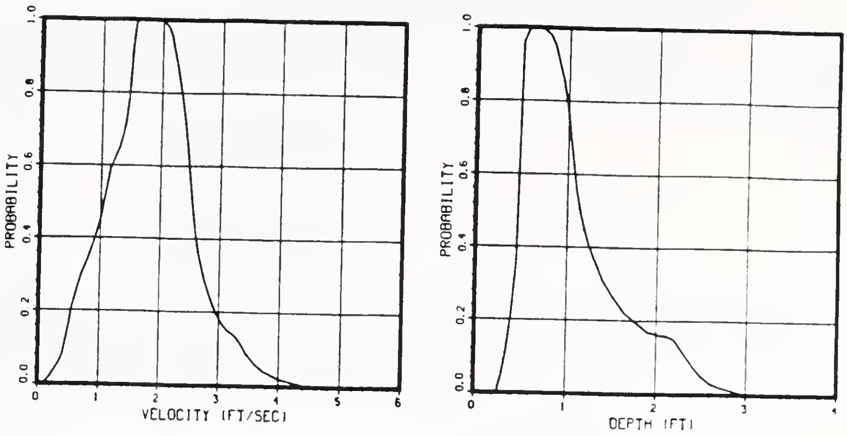

Figure 1. Probability of use criteria curves for brown trout spawning (from Bovee 1978).

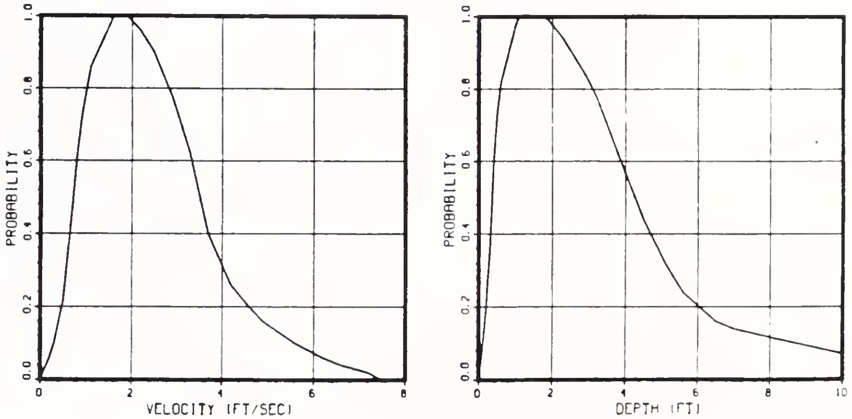

Figure 2. Probability of use criteria curves for brown trout egg incubation (from Bovee 1978).

# E. RIFFLE COMMUNITY METABOLISM STUDY

[illegible]

[illegible]

# The Use of Riffle Community Metabolism as a Measure of Water Quality Degradation in the Clark Fork River, Montana

## Final Report

by

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Abstract:

Using plexiglass metabolism chambers, community metabolism was measured at four riffle sites in the Clark Fork River during November, 1984, and April and August, 1985. To study the potential impacts of a kraft mill wastewater discharge on community metabolism, two riffle sites were sampled above the kraft mill outfall and two riffle sites were sampled below an established "mixing zone" for the kraft mill wastewaters.

The kraft mill discharge program had no effect on the metabolic rates of the riffle communities downstream of the mixing zone. The high background nutrient concentrations in this reach of the Clark Fork River supported high metabolic rates which minimized the impact of the kraft mill on riffle community metabolism. Enhanced metabolic rates at the most upstream riffle site (Flat Valley) suggested that an upstream source(s) of nutrients was affecting the metabolism of the river below Missoula. Moreover, groundwater flows in the area were found to be contributing nitrate to the Bitterroot and Clark Fork Rivers. During August, these groundwater subsidies supported high primary productivity rates which were phosphorus-limited. In areas not receiving groundwater (or point source) nitrate subsidies, riverine primary productivity was nitrate-limited.

During August of 1985, water column metabolism was measured at the four riffle sites using light-dark bottle incubations. No water column metabolism was detected at any of the riffle sites.

During an in situ chamber experiment, a 1:1 mixture of kraft mill wastewater and river water reduced primary productivity of the enclosed benthic community. The 1:1 mixture did not affect the diel respiration of the enclosed benthic community.

In an in situ light-dark bottle experiment, river water and three mixtures (1:1, 1:20, and 1:200) of kraft mill wastewater and river water were incubated to assess the impact of kraft mill wastewater on water column (vs benthic) metabolism. No water column metabolism was measured in the river water. Primary productivity was measured in all the mixtures of kraft mill wastewater and river water. Respiration was noted only in the 1:1 and 1:20 mixtures of kraft mill wastewater and river water. The changes in water column metabolism due to the addition of kraft mill wastewater were negligible when compared to the benthic community metabolism of the Clark Fork River.

# Acknowledgements

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# INRODUCTION

During 1984, Champion International modified the wastewater discharge program of its kraft paper mill in Frenchtown, Montana. Before this modification, the kraft mill used rapid infiltration basins as a final treatment for most (65%) of its wastewater (Grimestad 1977). The remaining wastewater (35%) was stored in holding ponds until the spring freshet of the Clark Fork River occurred; then the holding ponds were drained directly into the Clark Fork River. Eventually the rapid infiltration basins became clogged so that less wastewater was disposed by this method and the kraft mill began to experience storage problems. Champion International received permission from the Montana Department of Health and Environmental Sciences to modify the wastewater discharge program in April of 1984. Thereafter, the kraft mill began year-round direct discharge of its wastewater into the Clark Fork River. This year-round direct discharge program was subjected to some key restrictions to protect the water quality of the river. For example, direct discharge was not permitted when the river flowed less than 1900 cubic feet per second; or when ambient dissolved oxygen concentrations were less than 7.0 mg $l^{-1}$.

Despite these restrictions, the modification of the wastewater discharge program created much public concern about the potential environmental impacts of the kraft mill wastewater on the Clark Fork River. Two fish kills had been documented in the Clark Fork River that were attributed to the discharge of kraft mill wastewater during the late 1950's and early 1960's (Spindler and Whitney 1960; Shewman et al. 1984). These fish kills raised public concern about the toxicity of the wastewater. Because wood fibers contain relatively small amounts of phosphorus and nitrogen, the kraft mill would have to add large amounts of these nutrients to the wastewater to promote biological treatment in order to meet the five-day biological oxygen demand (BOD5) criteria specified by the Montana Department of Health and Environmental Sciences for the year-round direct discharge program (Shewman et al. 1984). There was public concern that this addition of nutrients might lead to a discharge of excess nutrients to the Clark Fork River which could cause eutrophication--an undesirable increase in autotrophic productivity of the periphyton (the attached algae on the river bottom)-- downstream of the kraft mill outfall.

The kraft mill was also allowed to increase it's annual loading of total suspended solids (TSS) to the river. Since 80-95% of the TSS was believed to be bacteria or bacterial cell fragments (Shewman et al. 1984), there was much concern that the increased loading of TSS would decrease dissolved oxygen concentrations of the river water or that the TSS would settle in pool areas of the river and cause other water quality problems.

To obtain information that would help address these public concerns, we designed a community metabolism study (cf. Bott et al. 1978) to examine the oxygen dynamics of the Clark Fork River. If the discharge of these bacterial cells exerted a significant impact on the Clark Fork River, the respiration (or the consumption of oxygen) of the riffle communities downstream of the kraft mill outfall would increase (cf. Boyle and Scott 1984). If the kraft mill wastewater contained elevated concentrations of nutrients (phosphorus, nitrates, ammonia, etc.), the net community primary productivity of the riffle communities (which produces oxygen) downstream of the kraft mill outfall would also increase (cf. Stockner and Shortreed 1978; Elwood et al. 1981; Peterson et al. 1983, 1985). Conversely, if the kraft mill wastewater contained significant concentrations of toxic substances, the net community primary productivity and respiration of the riffle communities downstream of the kraft mill outfall would be expected to decrease (Moore and Love 1977). For readers unfamiliar with measurement of community metabolism in rivers, a more detailed, explanatory text is included as Appendix A.

To detect these possible trends in the Clark Fork River, short-term field surveys (referred to as synoptic studies) were initiated for selected riffle areas above and below the kraft mill outfall. These synoptic studies involved intensive field efforts over a period of several days during autumn, 1984, and spring and summer, 1985, since community metabolism could change seasonally (Hall 1972; Minshall et al. 1983; Bott et al. 1985).

Since the Clark Fork River is subjected to other pollution sources upstream of the kraft mill (e.g. mining, a large municipal wastewater discharge, logging, agriculture), an experimental program also was developed to directly assess the impacts of kraft mill wastewater on: 1) the riffle community metabolism of the Clark Fork River; and 2) the water column metabolism of the Clark Fork River. In an attempt to obtain correlates of important water quality variables (e.g. phosphorus, nitrogen, chloride, sulfates, etc.) with expected trends in riffle community metabolism, water samples were collected during the synoptic studies and also during the experimental work. These samples were analyzed for several chemistry variables.

## OBJECTIVES

With the synoptic studies and the experimentalprogram, we hoped to accomplish the following five objectives:

1)To assess the impact of the year-round direct discharge program of the Frenchtown kraft mill on the riffle community metabolism of the Clark Fork River;

2) To document seasonal changes in the metabolic rates of the riffle communities in the Clark Fork River;

3) To assess the immediate impact of diluted kraft mill wastewater (1:1) on the riffle community metabolism of the Clark Fork River;

4) To determine the decomposition rate of diluted kraft mill wastewater (1:1, 1:20, and 1:200) in the Clark Fork River; and

5) To assess the feasibility of using riffle community metabolism as an indicator of such pollution.

## STUDY AREA

### Hydrogeology

The Clark Fork River, which originates near the city of Butte, drains the west slope of the Continental Divide in west-central Montana and eventually empties into the Columbia River via Lake Pend Oreille and the Pend Oreille River. About 160 km (1.0 km is 0.62 miles) from its origin, the river flows across bedrock at Hellgate Canyon and enters the northeast corner of the Missoula Valley.

After entering the Missoula Valley, the Clark Fork River flows southwesterly about 6 miles with an average stream gradient (a decrease of river elevation with distance) of 12 feet per mile before its confluence with the Bitterroot River about 4 miles west of Missoula (Figure 1.). The Bitterroot River has an average gradient of 6 feet per mile from where it enters the southeast corner of the Missoula Valley to the confluence (Geldon 1979). After the Clark Fork River meets the Bitterroot River, the river flows northwesterly until it

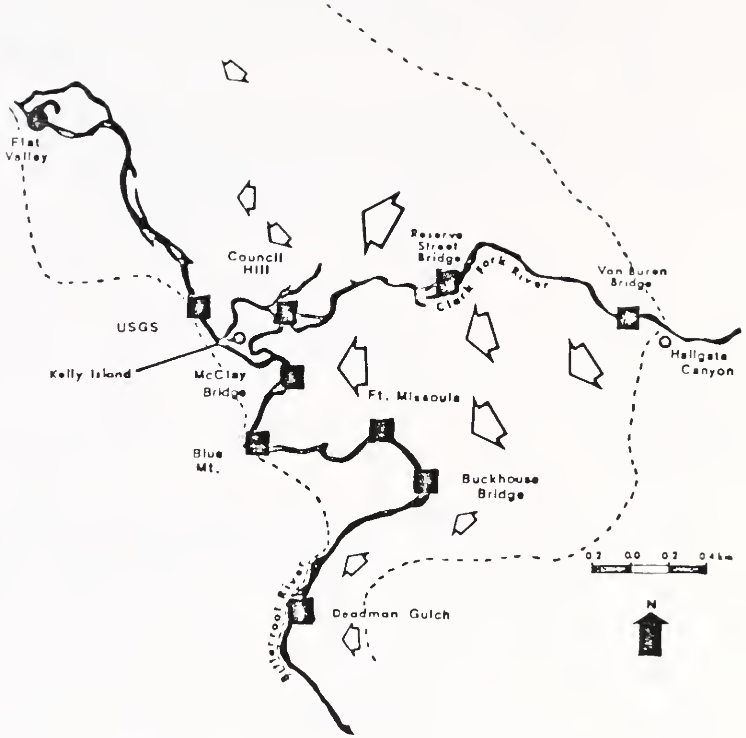

Figure 1. General direction of groundwater flow (see arrows) from the Clark Fork River above its confluence with the Bitterroot River to the Bitterroot River; and to the Clark Fork River below Kelly Island. Directions are based on piezometric contours of Gelman and Curry (1978). The circle is the location of the Flat Valley synoptic study site. The squares are the locations of sites sampled during a special nitrate study (see text). The stars are the locations of Hellgate Canyon and Kelly Island. The dotted line is the approximate boundary of groundwater storage in the Missoula Valley.

leaves the Missoula Valley at the Alberton Narrows (located about 16 km downstream of the Petty Creek Fishing Access), where it flows over bedrock again. (Konizeski and Alt 1972).

Within the Missoula Valley, the Clark Fork River is believed to be influent (i.e. river water infiltrates into the groundwater) from Hellgate Canyon to its confluence with the Bitterroot River (McMurtrey et al. 1965). From the confluence of the Bitterroot River with the Clark Fork River to the Alberton Narrows, the Clark Fork River is believed to be effluent (i.e. groundwater flows into the river) except for brief periods during the spring freshet (McMurtrey et al. 1965; Grimestad 1977). The Clark Fork River water that infiltrates into the groundwater near Hellgate Canyon apparently moves outward from the Clark Fork River and eventually empties into the Bitterroot River near Missoula (see Figure 1.) or into the Clark Fork River downstream of Kelly Island (Geldon and Curry 1978; Geldon 1979).

The Clark Fork River has a large influence on groundwater flow patterns in the Missoula Valley because the valley is filled with unconsolidated material (e.g. loose sand or gravel) that is highly porous. The amount of precipitation percolating through the soil and reaching the water table varies seasonally due to evaporation and plant transpiration. During January and February, all of the precipitation falling on the valley may potentially reach the water table. From April to October, little or no precipitation reaches the groundwater (Geldon 1979) so that the groundwater is recharged almost entirely by river water.

## Climate

The city of Missoula receives an average annual precipitation of 13 inches (33 cm). May and June are normally the wettest months and March is the driest month. The mountain peaks surrounding the city may receive up to 60 inches (152 cm) annually (Geldon 1979).

During the study period, drought conditions prevailed from May through July of 1985. This drought was followed by a period of heavy precipitation during August and September of 1985.

The average temperature in January, the coldest month, is 22.7°F (-5.2°C) indicating that most of the precipitation during this month will be snow. In July, the warmest month, the average temperature is 71.8°F (22.1°C) (Geldon 1979).

## Seasonal Variations of Water Quality in the Clark Fork River

The Clark Fork River is a dynamic system. Some physiochemical and biological characteristics change unpredictably, but other physiochemical and biological characteristics change temporally (and spatially) in a predictable manner. The interactions of climate, geology, and vegetation cause predictable seasonal changes in the flow of the Clark Fork River (Figure 2.). During most of the year, the average flow of the Clark Fork River remains at about 2000 to 3000 cubic feet per second (cfs) at the USGS gaging

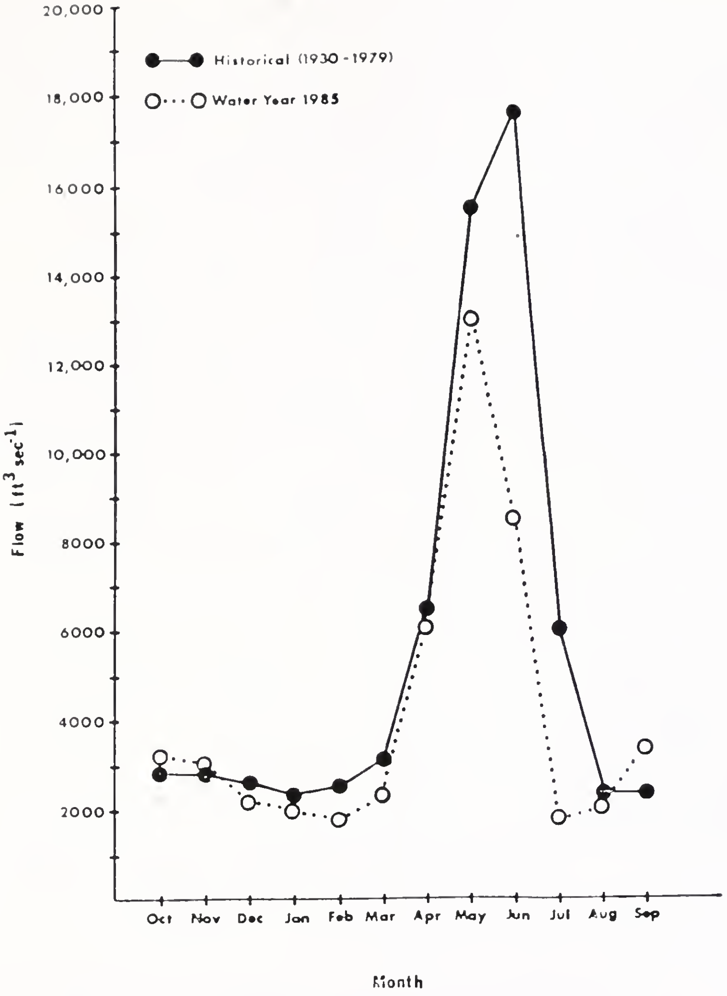

Figure 2. The historical (1930-1979) mean monthly flows of the Clark Fork River at the USGS gaging station below Missoula (Shewman et al. 1984). The 1985 (water year) mean monthly flows of the Clark Fork River at the USGS gaging station below Missoula (provisional data, USGS) are also given.

station below Missoula (see Figure 1.). During the spring freshet, the flow rapidly increases to an average of about 18,000 cfs. This increased flow is caused by melting snow and the increased precipitation which occurs during spring and early summer. This increased flow changes the water quality characteristics of the Clark Fork River.

During the spring freshet, the sediment load of the Clark Fork River increases (USGS 1979, 1980, 1981, 1982). This sediment is derived from material originally eroded from the watershed by 1) sheet, rill, and gully erosion due to overland flow; 2) mass wasting (e.g. landslides); and 3) river bank erosion (Dunn and Leopold 1978; Simons et al. 1979). Within the river channel, however, the increased erosive power of the river, due to the increased flow of the spring freshet, causes material (some previously deposited in the river) to be scoured and transported downstream (cf. Richards 1982). Some of the streambed material is resuspended and other material, which cannot be resuspended, is pushed and rolled downstream in a material flow known as bedload (Dunne and Leopold 1978). In addition, the Clark Fork River spills over its usual banks and scours material from the inundated floodplain (which is part of the stream channel during freshet) with the onset of the spring runoff. These erosional processes cause the total suspended solids (TSS) concentration, the dissolved organic carbon (DOC) concentrations, and the total suspended organic carbon concentrations to increase with increasing flow, as has been noted in the limited water quality data collected at the USGS gaging station below Missoula (USGS 1979, 1980, 1981, 1982). In contrast, as the river flow increases, alkalinity, hardness, specific conductance, and the concentrations of nitrate ($NO_3$), dissolved silica ($SiO_2$), dissolved sulfate ($SO_4$), dissolved sodium (Na), dissolved magnesium (Mg), dissolved calcium (Ca), and dissolved solids concentrations decrease (USGS 1979, 1980, 1981, 1982) due to dilution. As the flood waters of the spring freshet recede, most of the suspended solids are deposited on the floodplain and in the slower moving portions of the river.

Besides seasonal variations, there are also long-term, year-to-year variations in water quality and quantity of the Clark Fork River. Water quality problems that occur in some years may not be present in other years (e.g. dewatering of the river for irrigation purposes during droughts). In addition to the seasonal and year-to-year variations described above, the water quality of the Clark Fork River also changes due to watershed disturbances.

## Disturbances in the Clark Fork River Watershed

Extensive mining of copper, gold, and phosphorous has occurred near the headwaters of the Clark Fork River. Tailings from some of these mining operations are in the floodplain of the river. During the spring freshet, some of these tailings are eroded downstream and cause increased concentrations of copper and other heavy metals in the Clark Fork downstream. Some of these tailings have settled in the reservoir behind the Montana Power Company hydroelectric dam near Milltown, Montana (Bailey 1976). Heavy metals from these sediments are apparently contaminating the groundwater in the Milltown area (Woessner et al. 1984).

Nutrients and organic matter are added to the Clark Fork River from a variety of sources. Treated wastewater is discharged into the Clark Fork River by many municipalities along the river. The kraft paper mill in Frenchtown and a meat-packing plant in Missoula have also added significant contributions of nutrients and organic matter to the river (USEPA 1974). Wood waste, apparently from sawmills in Bonner and Missoula during the 1950's, has been recorded in the Clark Fork River (Spindler 1959). Agricultural practices and logging activities may also add nutrients, sediments, and organic matter to the river.

The disturbance of fire has always occurred in the Clark Fork watershed. During the summer, hundreds of lightning strikes may occur in Montana within a 24-hour period and some of these lightning strikes will cause fires. Other fires are caused by people. Historically, the Native Americans in the area intentionally burned areas during autumn to aid hunting, food plant production, and horse grazing (Barrett 1981). Contradictory evidence exists about the effects of wildfire on the water quality of lakes and streams. Tiedemann et al. (1978) found that a wildfire in eastern Washington state increased nutrient loadings to a local stream. In Minnesota, however, wildfire may not impact the water quality of local lakes and streams because nutrients are immobilized in the soil and by prolific post-fire vegetation (McColl and Grigal 1977). Hence, the effects of fires that occurred during the present study, the Hellgate Canyon fire in July, 1985 and a fire at Ninemile in August, 1985, on the water quality of the Clark Fork River remain speculative.

Other disturbances in the Clark Fork River watershed include alterations of the river channel and riprapping river banks due to construction of Interstate 90 (Weisel 1972), and urbanization. When analyzing the impact of the kraft mill on the Clark Fork River, the effects of these other disturbances to water quality must also be considered.

## Location of Study Sites

The Champion International kraft paper mill and the study sites are located in the Missoula Valley downstream of the confluence of the Bitterroot River with the Clark Fork River in western Montana (Figure 3.). The kraft mill is located approximately 24 km from Missoula, near the village of Frenchtown.

To study the impacts of the kraft mill on the river, community metabolism measurements were taken at four riffle sites in the Clark Fork River (Figure 3.). Two riffle sites, we call Flat Valley and Harper's Bridge, were located upstream of the kraft mill outfall. Note, however, that the

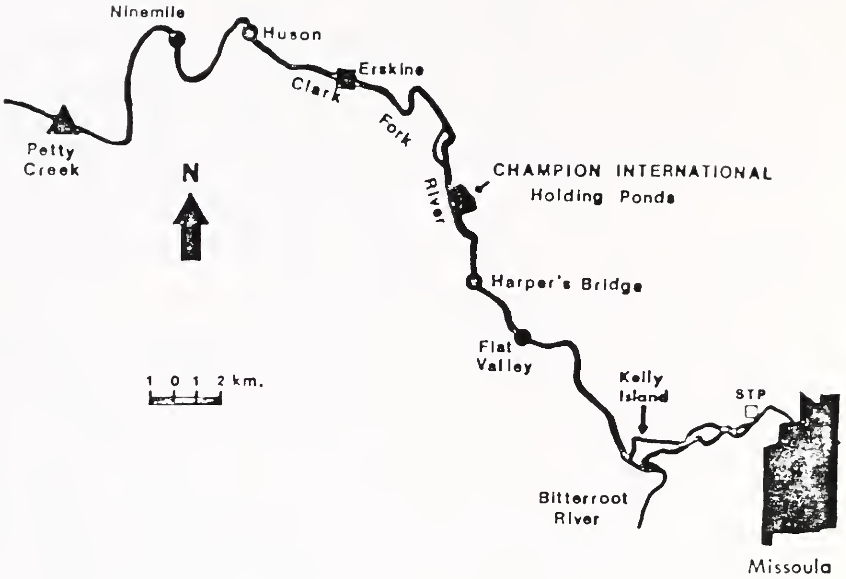

Figure 3. Study sites on the Clark Fork River with reference to the kraft mill (Champion International), Kelly Island, and the Missoula sewage treatment plant (STP). The circles are locations of the synoptic study sites. The triangle is the location of the experimental work. The square is the location of a site sampled during a special nitrate study (see text).

sites were located downstream of the Missoula sewage treatment plant, which adds secondary treated wastewater to the river. This was done to isolate the impact of the kraft mill from the impact of the sewage treatment plant on the Clark Fork River. The other two riffle sites, called Huson and Ninemile, were located downstream of the mixing zone for the kraft mill wastewater as determined by the Montana Department of Health and Environmental Sciences (Dr. Loren

Bahls, Montana Water Quality Bureau (MWQB), pers. communication).

The Flat Valley site is located 3 to 5 km upstream from Harper's Bridge. It is accessible from the Big Flat Road on the south side of the Clark Fork River.

The Harper's Bridge site is located 100 to 150 meters downstream from Harper's Bridge.

The Huson site is located about 200 to 300 meters downstream from the railroad bridge crossing the Clark Fork River near Huson. Most of the year, this site is accessible only by boat or canoe.

The Ninemile site is located about 0.5 to 1.0 kilometer downstream from where Interstate 90 crosses the Clark Fork River and about 1.5 to 2.0 kilometers upstream from the confluence of the Clark Fork River with Ninemile Creek.

When comparing the dissolved oxygen concentrations of their sampling sites in the Clark Fork River below the kraft mill, the Montana Water Quality Bureau noted relatively lower dissolved oxygen concentrations at the Petty Creek Fishing Access during the summer of 1984. To obtain more information about this "oxygen sag", a riffle site at the Petty Creek Fishing Access was chosen as an additional site for the *in situ* experimental studies. This riffle site is located in the Clark Fork River about 100 to 200 meters upstream of the confluence of the Clark Fork River with Petty Creek.

# METHODS AND MATERIALS

## Synoptic Studies

At each of the four sampling sites (Figure 3.), samples of river bottom rubble and associated biota (known as benthos) were enclosed in 4 plexiglass metabolism chambers. Then, each chamber was filled with river water and submersed near shore. Four identical chambers were used at each site for statistical replication. Changes in dissolved oxygen concentrations were then recorded over a 24 hour (diel) period with a YSI dissolved oxygen probe. During the day, these dissolved oxygen concentrations were recorded every 15 to 30 minutes. During the night, measurements were recorded only every 1.0 to 2.0 hours. The chambers were flushed periodically to keep the temperature and dissolved oxygen concentrations of the chambers within 2°C and 2.0 ppm of the ambient river temperature and dissolved oxygen concentrations, respectively, and to replenish nutrients which might have been depleted during the incubation period. After the sampling period, the river water in each chamber was drained and the water volume was recorded. The net community primary productivity (production of organic matter and oxygen) was then determined from the sum of the positive diel changes in oxygen concentrations (Bott et al. 1978) and converted to carbon units using the equation in Table 1. An average respiration rate (mg $O_2$ $hr^{-1}$) was determined from the

Table 1. Equation used to convert changes in dissolved oxygen concentrations into production or consumption of organic matter (carbon) per area of stream bottom.

$$\frac{\text{mg C}}{\text{m}^2} = \frac{\text{mg O}_2}{1} * \frac{12\text{ mg C}}{32\text{ mg O}_2} * L * \frac{1}{A}$$

where:

mg C = milligrams of carbon produced or consumed per day

mg $O_2$ = milligrams of dissolved oxygen produced or consumed per day

$m^2$ = square meter

1 = liter

L = volume of river water in chamber (liters)

A = photosynthetic surface area of chamber ($0.125 m^2$)

night-time decreases of dissolved oxygen. This respiration rate was assumed to be constant throughout the diel period (Odum 1956) so that diel respiration ($R_{24}$) was determined by multiplying the respiration rate by 24 hours. Respiration during the photoperiod ($R_{pp}$) was determined by multiplying the average respiration rate by the length of the daylight period. The units of respiration were converted from mg $O_2$ to mg C $m^{-2}$ $day^{-1}$ using the equation in Table 1. Gross primary productivity, net daily metabolism, and the P:R ratios were calculated from the respiration and net community primary productivity measurements (Naiman 1983) using the following equations:

1) Gross primary production (GPP) = net community primary production (NCPP) + respiration during the photoperiod ($R_{pp}$). Gross primary production is a measure of how much organic matter would be produced by photosynthesis if respiration was not occurring simultaneously.

2) Net daily metabolism (NDM) = GPP - $R_{24}$.

3) Photosynthesis/Respiration (P:R) ratio = GPP/$R_{24}$.

During the diel sampling period, several physical variables of the riverine environment were also measured to determine their influence on concomitant community metabolism. Conductivity and water temperature were measured hourly with a YSI S-C-T conductivity meter. Stream velocity near the point of benthos collection was measured every four to six hours with a Weathermeasure current meter or a General Oceanics current meter.

During November, photosynthetically active radiation (400 - 700 nm) was recorded every 15 minutes at each riffle site with a Li-Cor 188 light meter and a quantum probe. Due to logistical problems with using the Li-Cor meter, a Kalsico photometer was used to record incident radiation every 15 minutes at each riffle site during April and August. Unfortunately, the Kalsico photometer measured light energy from a wider spectrum of wavelengths than the Li-Cor quantum probe so that comparisons of light energy between November and April or August were not possible. To determine daily insolation rates, the instantaneous light measurements were assumed to be constant for the entire 15 minutes between measurements and the insolations over the 15 minute intervals were summed for the length of daylight (known as photoperiod).

During the August synoptic run, a series of light-dark bottle incubations were run at each riffle site to measure the metabolism of the water column (APHA et al. 1981). Every 3 hours, four water samples were collected in clear BOD bottles and two water samples were collected in darkened BOD bottles using an antidiffusion device (cf. Hall 1970) to avoid introducing bubbles into the BOD bottles during collection. The initial dissolved oxygen (DO) concentrations were determined by immediately fixing two samples collected in the clear BOD bottles and then analyzing them later by the azide modification of the Winkler method (APHA et al. 1981). Two clear BOD bottles and the two darkened BOD bottles were placed on the river bottom for 3 hours and then were pulled out of the river and immediately fixed for later analysis of dissolved oxygen concentration. The differences between the initial and final dissolved oxygen concentrations were used to estimate the metabolism of the community in the water (vs. the benthos) as given in Hall and Moll (1975).

### Water Chemistry

To relate the riffle community metabolism data to the water quality of the Clark Fork River, duplicate water chemistry samples were taken from each riffle area on November 30, 1984, and August 5, 1985. No water chemistry samples were taken during the April synoptic run, due to the onset of the spring freshet. The changing river chemistry, due to the rising water, would have made comparisons to the metabolism data of the riffle sites meaningless.

The water samples were analyzed at the Flathead Lake Biological Station for the water chemistry variables listed in Table 2. Most of the water chemistry variables were analyzed following the Environmental Protection Agency's NPDES approved procedures (USEPA 1983) as specified in Table 2. Dissolved organic carbon and particulate organic carbon were analyzed by an Oceanography International Corp. Total Carbon System (TCS) following procedures suggested by Menzel and Vaccaro (1964). Nitrate, nitrite, chloride, and sulfate were analyzed simultaneously using a Dionex Ion Chromatograph 16 (IC) (Dionex Corp. 1979; Rawa 1979).

### Experimental Program: Effect of Diluted Kraft Mill Wastewater on Benthic Riffle Community Metabolism

To assess the acute impact of the kraft mill wastewater on the metabolism of the Clark Fork River riffle communities, an *in situ* chamber experiment (i.e. experiments which

Table 2. Methods for the measurement of water chemistry variables. Source: USEPA 1983.

| Variables | Methods |
|---|---|
| Turbidity | EPA 180.1 |
| Hardness | |
| Calcium (Ca) | EPA 215.1 |
| Magnesium (Mg) | EPA 242.1 |
| Soluble Reactive Phosphorus ($PO_4$-P) | EPA 365.3 |
| Total Phosphorus (TP) | EPA 365.3 |
| Ammonia ($NH_3$-N) | EPA 350.2 |
| Total Kjeldahl Nitrogen (TKN) | EPA 351.3 |
| Nitrate ($NO_3$-N) and nitrite ($NO_2$-N) | IC[1] |
| Dissolved silica ($SiO_2$) | EPA 370.1 |
| Chloride (Cl) | IC[1] |
| Sulfate ($SO_4$-S) | IC[1] |
| Dissolved organic carbon (DOC) | TCS[2] |
| Particulate organic carbon (POC) | TCS[2] |
| Alkalinity | EPA 310.1 |
| Sodium (Na) | EPA 273.2 |

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[1] IC refers to the Dionex Ion Chromatograph 16.

[2] TCS refers to the Oceanography International Total Carbon System.

occurred in the Clark Fork River) and a water column metabolism experiment were developed. The kraft mill wastewater used in the experiment was collected from the last holding pond (Pond 13A) before the wastewater was discharged directly into the Clark Fork River.

In the chamber experiment, samples of Clark Fork River benthos were collected from the riffle area at the Petty Creek Fishing Access and were enclosed in six metabolism chambers. Instead of filling the chambers with river water, as in the synoptic studies, diluted kraft mill wastewater was introduced into the chambers through the port for the dissolved oxygen probe via a special delivery system. Using this modification, three chambers were dosed with Clark Fork River water (the control) and three chambers were dosed with a 1:1 mixture of kraft mill wastewater and river water (the treatment). Dissolved oxygen concentrations in the chambers were recorded over a 24-hour period in a manner similar to that used in the synoptic studies, except that in this case, the metabolism chambers were periodically flushed with the appropriate treatment rather than with river water. During the experiment, incident radiation was recorded every 15 minutes with a Kalsico photometer.

## Experimental Program: Effect of Diluted Kraft Mill Wastewater on Water Column (vs Benthic) Metabolism

To assess the influence of different concentrations of the kraft mill wastewater on metabolism of the river water column, a series of light-dark bottle incubations were conducted with three mixtures (1:1, 1:20, 1:200--parts wastewater:parts river water) of kraft mill wastewater and

Clark Fork River water collected at the Petty Creek Fishing Access (the treatments). Similarly, Clark Fork River water collected at the Petty Creek Fishing Access were also incubated as a control. For each of the three treatments and the control, light-dark bottle incubations were conducted as described previously, except this time, the dissolved oxygen concentrations of the solutions in the BOD bottles were determined with a YSI dissolved oxygen probe while the samples were mixed with a stir bar. Before recording dissolved oxygen concentrations, the YSI dissolved oxygen probe was standardized against a dissolved oxygen value measured by the Winkler method (APHA 1981). The incubations for all treatments occurred simultaneously.

The metabolism variables were estimated from the changes in dissolved oxygen concentrations as previously described. Diel respiration was assumed to be due solely to the decomposition of organic matter contained in the kraft mill wastewater.

## RESULTS AND DISCUSSION

### Seasonal Changes in Metabolic Rates

Significant ($p << 0.001$) seasonal variations in these riffle community metabolism variables were noted for the Clark Fork River (Tables 3. and 4.). Net community primary

Table 3. Comparison of metabolism variables measured during the synoptic study. Data are means; standard deviations are given in parentheses.

| Parameter | Date | Flat Valley | Harper's Bridge | Huson | Ninemile |
|---|---|---|---|---|---|
| Net Community Primary Productivity (mg C $m^{-2}$ $day^{-1}$) | Nov. | 420[2] (70) | 520 (210) | 420 (100) | 460 (170) |
| | Apr. | 1380 (280) | 810 (150) | 840 (120) | 1000 (110) |
| | Aug. | 2530 (350) | 1920 (480) | 2340 (350) | 1450 (110) |
| Diel Respiration (mg C $m^{-2}$ $day^{-1}$) | Nov. | 590[2] (60) | 830 (150) | 780 (110) | 800 (220) |
| | Apr. | 950 (120) | 740 (40) | 380 (40) | 500 (70) |
| | Aug. | 1570 (90) | 1300 (140) | 1140 (160) | 1170 (90) |
| Gross Primary Productivity (mg C $m^{-2}$ $day^{-1}$) | Nov. | 600[2] (70) | 780 (250) | 660 (110) | 710 (120) |
| | Apr. | 2000 (360) | 1200 (160) | 1100 (140) | 1300 (120) |
| | Aug. | 3500 (400) | 2740 (450) | 3030 (450) | 2150 (130) |
| Net Daily Metabolism (mg C $m^{-2}$ $day^{-1}$) | Nov. | + 10[2] | − 50 | − 120 | − 90 |
| | Apr. | +1050 | + 460 | + 720 | + 800 |
| | Aug. | +1930 | +1440 | +1890 | + 980 |
| P:R[1] | Nov. | 1.02 | 0.94 | 0.85 | 0.89 |
| | Apr. | 2.10 | 1.62 | 2.89 | 2.60 |
| | Aug. | 2.23 | 2.11 | 2.66 | 1.84 |

[1] Gross Primary Productivity/Diel Respiration

[2] value believed to be abnormally low—see text

productivity (NCPP) increased 3X to 6X from November to August (Figure 4.). The variability among net community primary productivity measurements recorded at the same riffle sites also increased from November to August (note the standard deviations in Table 3.). This situation, common in growth measurement studies, caused problems in satisfying the basic assumptions of statistical analyses. These problems were resolved by transforming the data to common logarithms before statistical analysis (Sokal and Rolhf 1969). Gross primary productivity (GPP) followed the same trends as net community primary productivity (Figure 5.), indicating the importance of autochthonous inputs of energy to the energy budget of the Clark Fork River. The seasonal increases in net community primary productivity and gross primary productivity were probably due to the seasonal increases in

Table 4. Multiple comparisons among seasons of the community metabolism variables pooled for all sites using the Student-Newman-Keuls test (Sokal and Rohlf 1969). Respiration ($R_{24}$) data are means (mg C $m^{-2}$ $day^{-1}$). Net community primary productivity (NCPP) and gross primary productivity (GPP) data are means after logarithmic transformations. These means are all significantly ($p < 0.05$) different.

Log (NCPP)

| | | | | |
|---|---|---|---|---|
| 3.2656 | > | 2.9400 | > | 2.6462 |
| Aug. | | Apr. | | Nov. |

$R_{24}$

| | | | | |
|---|---|---|---|---|
| 1200 | > | 810 | > | 540 |
| Aug. | | Nov. | | Apr. |

Log (GPP)

| | | | | |
|---|---|---|---|---|
| 3.414 | > | 3.0755 | > | 2.8556 |
| Aug. | | Apr. | | Nov. |

the photoperiod (Table 5.) and in stream temperatures (Table 6.). The general decreases in stream velocity (Table 7.) from November to August, measured in the areas where the benthos samples were obtained, might have also influenced the primary productivity rates (cf. Whitford and Schumacher 1961;

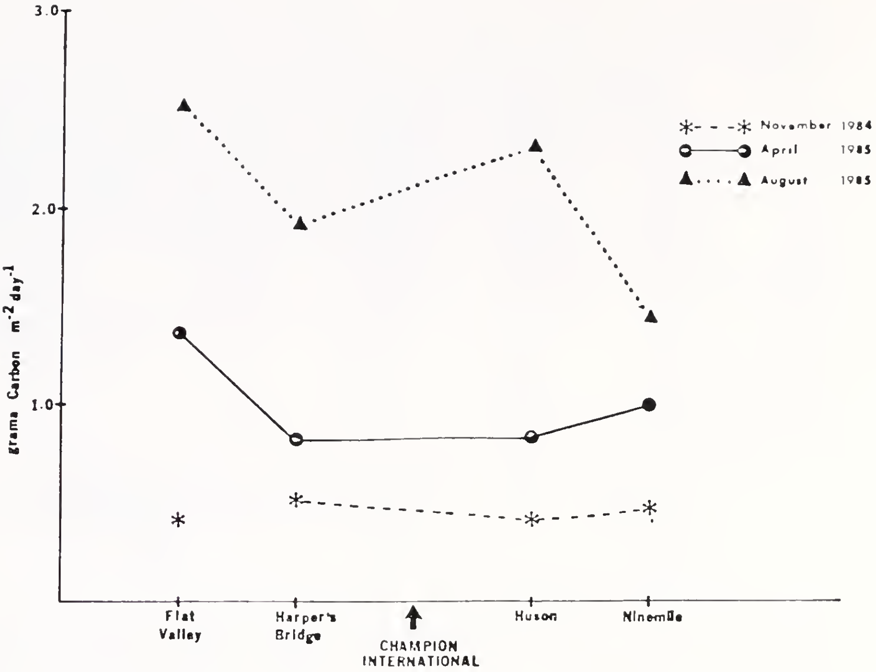

Figure 4. Net community primary productivity observed at e four sites where synoptic metabolism studies w e conducted (see Figure 3.).

Horner and Welch 1981; Nowell and Jumars 1984), but a c er comparison of the measured stream velocities to the corresponding primary productivity rates (Table 3.) indicated that these influences were secondary to the influences of photoperiod and stream temperatures on primary productivity.

Diel respiration ($R_{24}$) decreased from November to April, but then increased in August 2X to 3X the diel respiration in April (Figure 6.). Unlike the primary productivity measurements, the variablilty among diel respiration measurements did not increase as the means increased, so

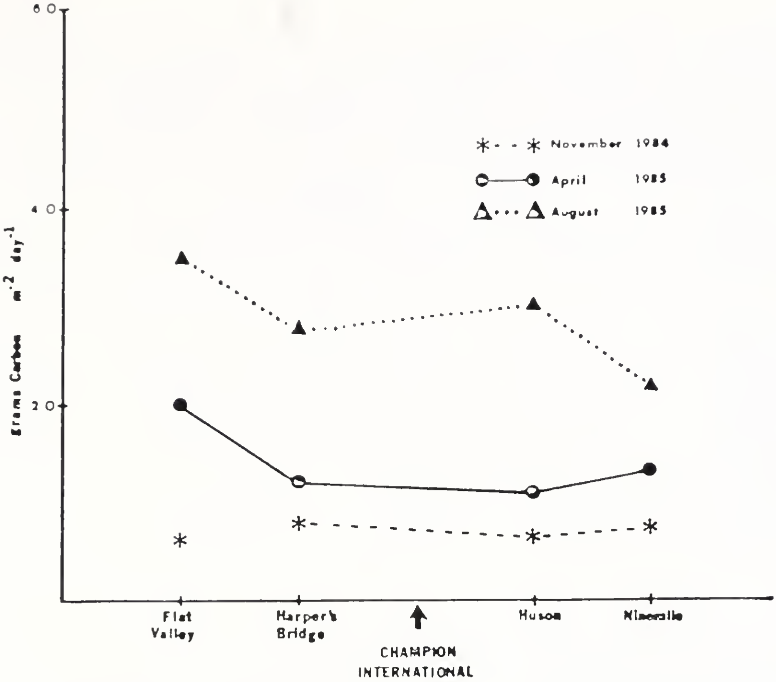

Figure 5. Gross primary productivity observed at the four sites where synoptic metabolism studies were conducted (see Figure 3.).

these data were not transformed before conducting tests of significance. The decrease in diel metabolism from November to April was probably due to decomposition of organic matter during autumn and winter; scouring of the river bottom by ice during winter (cf. Hynes 1970); and scouring by moving rock material (bedload) during the onset of the spring freshet. The increase in diel respiration noted from April to August was probably due to the accumulation of organic matter, primarily from algal photosynthesis, and the increase in stream temperatures.

Table 5. Comparison of photoperiod (hours) measured in the field during the synoptic studies.

| Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|
| Nov. | 8.5 | 9.0 | 9.5 | 9.75 |
| Apr. | 15.0 | 13.75 | 14.0 | 14.75 |
| Aug. | 14.75 | 15.25 | 14.75 | 14.25 |

Table 6. Comparison of the means of stream temperatures (°C) measured in the field during the synoptic studies. Ranges are given in parentheses.

| Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|
| Nov. 1984 | 2.6<br>(2.0-3.7) | 2.5<br>(1.6-3.4) | 1.6<br>(1.0-2.5) | 3.2<br>(2.5-3.9) |
| Apr. 1985 | 12.3<br>(11.1-13.5) | 10.9<br>(10.1-12.4) | 10.0<br>(8.3-11.5) | 8.3<br>(7.4-10.3) |
| Aug. 1985 | 16.2<br>(13.9-18.4) | 18.0<br>(16.1-19.8) | 16.0<br>(14.3-17.7) | 18.8<br>(15.8-22.2) |

Table 7. Comparison of mean stream velocities (cm $sec^{-1}$) measured in the field during the synoptic studies. Ranges are given in parentheses.

| Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|
| Nov. | 114<br>(104-125) | 87<br>(67-97) | 97<br>(59-131) | 62<br>(26-101) |
| Apr. | 50<br>(32-68) | 50<br>(35-67) | 60<br>(41-74) | 14<br>(8-20) |
| Aug. | 34<br>(13-64) | 12<br>(5-21) | 36<br>(23-48) | 33<br>(24-42) |

Note that the diel respiration at Flat Valley did not decrease from November to April. The November set of metabolism measurements at Flat Valley was not included in the tests of significance because the volumes of river water used in the metabolism chambers were not recorded. Previous work with metabolism chambers at the Biological Station had indicated that the variation in water volume within the chambers was negligible and did not affect the interpretation of metabolism results. After the Flat Valley metabolism data were collected, it was suspected that the variation in water volume might be important to this study so the water volumes were recorded for the rest of the study. An average water volume was calculated from the recorded water volumes of chambers at the other sites during November and this average

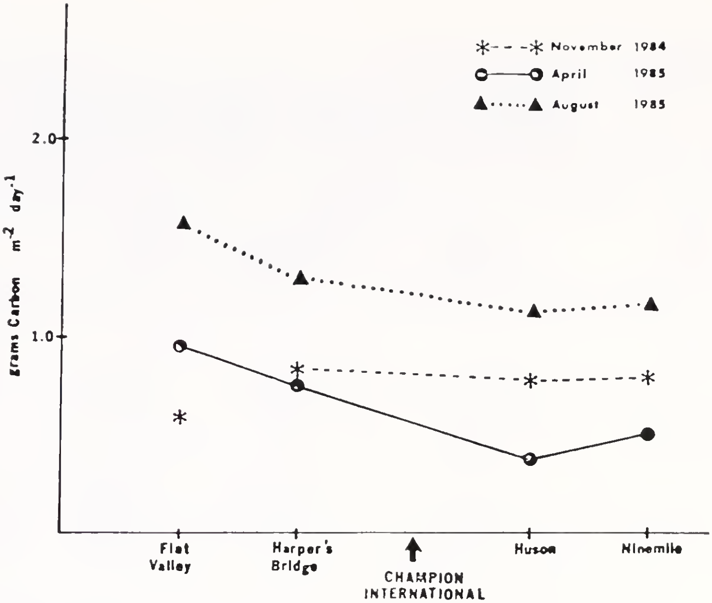

Figure 6. Diel respiration observed at the four sites where synoptic metabolism studies were conducted (see Figure 3.).

was used to obtain the metabolism values at Flat Valley during November. This average might have underestimated the true productivity and respiration rates for Flat Valley during November. The P:R ratio, which was not dependent upon the water volume within the chambers, was a true independent metabolism measurement for Flat Valley.

Negative net daily metabolism values and the P:R ratios indicated a predominance of respiration over primary productivity during November at all sites except Flat Valley (Table 3.). In contrast, during April and August, primary productivity dominated respiration. These metabolism variables indicated that during spring and summer, the riffle sites were accumulating organic matter due to algal photosynthesis, but during autumn and winter, the riffle sites were losing organic matter.

The observed seasonal changes were comparable to the seasonal changes observed in an Idaho river (Minshall et al. 1983), but the magnitude of productivity and respiration were higher in the Clark Fork River than that observed in the Idaho river. One reason for this difference was that Minshall et al. (1983) reported estimates for the metabolism of the total benthic community whereas the values reported within this study were confined only to the riffle areas of the Clark Fork River. However, the high nitrogen and phosphorus concentrations of the Clark Fork River probably supported (and still support) a much higher primary productivity than most western U.S. rivers.

Trends in the community metabolism variables changed seasonally among the four riffle sites (Figures 4. - 6.) During November, there was no significant ($p > 0.05$) difference among riffle sites in net community primary productivity (NCPP), in gross primary productivity (GPP), or in diel respiration ($R_{24}$).

During April, Flat Valley had a significantly ($p < 0.05$) higher NCPP, GPP, and $R_{24}$ than the other three sites (Table 8.). Harper's Bridge had a significantly ($p < 0.05$) greater diel respiration than the sites downstream of the kraft mill, but the diel respiration was significantly ($p < 0.05$) less than Flat Valley.

Table 8. Multiple comparisons among riffle sites of the community metabolism variables during April, 1985, using the Student-Newman-Keuls test. Respiration ($R_{24}$) data are means (mg $m^{-2}$ $day^{-1}$). Net communityprimary productivity (NCPP) and gross primary productivity (GPP) are means after logarithmic transformation. Underlined means are not significantly ($p > 0.05$) different.

Log (NCPP)

| Flat Valley | Nine-mile | Huson | Harper's Bridge |
|---|---|---|---|
| 3.1322 | 2.9972 | 2.9185 | 2.9042 |
| | ———— | ———— | ———— |

$R_{24}$

| Flat Valley | Harper's Bridge | Nine-mile | Huson |
|---|---|---|---|
| 950 | 740 | 500 | 380 |
| | | ———— | ———— |

Log (GPP)

| Flat Valley | Nine-mile | Harper's Bridge | Huson |
|---|---|---|---|
| 3.2915 | 3.1157 | 3.0890 | 3.0217 |
| | ———— | ———— | ———— |

During August, the NCPP and GPP were significantly ($p < 0.05$) less at Ninemile than the other three riffle sites (Table 9.). Diel respiration was significantly ($p < 0.05$)

Table. 9. Multiple comparisons among riffle sites of community metabolism variables during August, 1985, using the Student-Newman-Keuls test. Respiration ($R_{24}$) data are means (mg $m^{-2}$ day$^{-1}$). Net community primary productivity (NCPP) and gross primary productivity (GPP) are means after logarithmic transformation. Underlined means are not significantly ($p > 0.05$) different.

Log (NCPP)

| Flat Valley | Huson | Harper's Bridge | Nine-mile |
|---|---|---|---|
| 3.3992 | 3.3647 | 3.2730 | 3.159 |
| ——— | ——— | ——— | |

$R_{24}$

| Flat Valley | Harper's Bridge | Nine-mile | Huson |
|---|---|---|---|
| 1570 | 1300 | 1170 | 1140 |
| | ——— | ——— | ——— |

Log (GPP)

| Flat Valley | Huson | Harper's Bridge | Nine-mile |
|---|---|---|---|
| 3.5414 | 3.4782 | 3.4337 | 3.3309 |
| | ——— | ——— | |
| ——— | ——— | | |

greater at Flat Valley than the other three riffle sites. The GPP at Huson was not significantly ($p > 0.05$) different from Flat Valley or Harper's Bridge, but GPP at Flat Valley was significantly ($p < 0.05$) greater than at Harper's Bridge. The NCPP at Harper's Bridge might have been underestimated, in part, because a short afternoon thunderstorm occurred during metabolism measurements. This caused a brief light limitation (Table 10.), which decreased primary productivity. The weather was clear during metabolism measurements at the other riffle sites during August.

During November and April, however, no correlations were found between the metabolism variables and daily incident radiation or photosynthetically active radiation. The lack of correlation during November might be due to the very cold temperatures restricting primary productivity. During April, the dynamic water quality characteristics of the river during the onset of the spring freshet might have obscured the influence of daily insolation on primary productivity.

In addition, no general correlations were found between the metabolism variables and specific conductance with one exception. During April and August, the Flat Valley site had the lowest conductivity (Table 11.) and the greatest metabolic rates.

Table 10. Comparison of daily insolation rates of photosynthetically active radiation (PAR) (einsteins $m^{-2}$ $day^{-1}$) and incident radiation ($X10^6$ Joules $m^{-2}$ $day^{-1}$) measured in the field during the synoptic studies. Concurrent weather conditions are also given: Clear (C), Mostly Clear (MC)[1], Partly Cloudy (PC)[2], and Overcast (OC)[3]. Changing weather conditions are indicated with a double entry for the affected riffle site.

| Variable | Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|---|
| Daily Insolation of PAR | Nov. | 13.3 | 8.10 | 6.52 | 8.44 |
| Daily Insolation of Incident Radiation | Apr. | 13.3 | 7.61 | 14.5 | 11.5 |
| | Aug. | 13.9 | 11.7 | 14.3 | 12.7 |
| Weather Conditions | Nov. | C-OC | PC-OC | OC | C-OC |
| | Apr. | C-PC | PC-OC | MC | PC-OC |
| | Aug. | MC | C | C | C |

[1] Cloud cover < 25%.

[2] Cloud cover 25 - 75%.

[3] Cloud cover > 75%.

## Impacts of the Kraft Mill on Riffle Community Metabolism of the Clark Fork River

Since there was generally no significant difference in NCPP, GPP, or $R_{24}$ between riffle sites located above the kraft mill and the riffle sites downstream of the mill,

Table 11. Comparison of mean specific conductances (umhos $cm^{-2}$) measured in the field during the synoptic studies. Conductivity values have been standardized to 25°C. Ranges are given in parentheses.

| Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|
| Nov. | 234<br>(226-240) | 262<br>(254-269) | 261<br>(255-270) | 256<br>(252-260) |
| Apr. | 164<br>(154-170) | 214<br>(199-222) | 179<br>(144-189) | 196<br>(186-200) |
| Aug. | 239<br>(232-248) | 248<br>(222-257) | 247<br>(231-250) | 271<br>(264-278) |

Table 12. Rate of wastewater direct discharge by kraft mill and flow of Clark Fork River at the U.S.G.S. station below Missoula during sampling of riffle sites in August.

| Parameter | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|
| Kraft Mill Wastewater Direct Discharge ($ft^3$ $sec^{-1}$) | 0.0 | 3.1 | 3.3 | 0.0 |
| Clark Fork River Flow at U.S.G.S. Station below Missoula ($ft^3$ $sec^{-1}$) | 1893 | 2528 | 2708 | 1947 |

neither a nutrient impact nor a toxic impact on riffle community metabolism was detected due to the addition of kraft mill wastewater to the Clark Fork River.

During August, no water column metabolism was detected at any of the synoptic study riffle sites. The kraft mill was not direct discharging wastewater during some of these measurements (Table 12.), but even when direct discharging did occur, no water column metabolism was detected. This low metabolism of the water column was substantiated by the low BOD5 and COD (chemical oxygen demand) concentrations measured by the Montana Water Quality Bureau (unpublished data, MWQB) for most of these sites (Flat Valley was not sampled by the Water Quality Bureau) during July 29-30, 1985. The BOD5 and COD concentrations at these sites were also low during other periods of the year. These results suggested that the changes of dissolved oxygen observed in the Clark Fork River were due to benthic metabolism processes and were not due to oxygen demands of suspended organic matter or dissolved organic matter in the river water. Hence, decomposition of the dissolved organic carbon (DOC) and particulate organic carbon (POC) of the wastewaters from the kraft mill or the Missoula sewage treatment plant were not directly depressing dissolved oxygen concentrations of the river water at these riffle sites.

Analysis of the chemical characteristics of the kraft mill wastewater (Table 13.) indicated that the elevated concentrations of soluble reactive phosphorus, total

Table 13. Comparison of kraft mill wastewater characteristics before secondary treatment and after secondary treatment of wastewater. Data for kraft mill wastewater before secondary treatment taken from the Final Environmental Impact Statement for the Proposed Expansion of the Hoerner-Waldorf Pulp and Paper Mill at Missoula, Montana (DHES 1974). Data for kraft mill wastewater after secondary treatment are means of duplicate samples collected on September 3, 1985.

| Parameter | Before Secondary Treatment (1971) | After Secondary Treatment (1985) |
|---|---|---|
| Turbidity (NTU) | 412 (t.u.) | 22.5 |
| Hardness (mg $CaCO_3$ $l^{-1}$) | --- | 215 |
| Ca (mg $l^{-1}$) | --- | 61.2 |
| Mg (mg $l^{-1}$) | --- | 15.2 |
| $PO_4$-P (mg $l^{-1}$) | 0.3 | 0.287 |
| TP (mg $l^{-1}$) | 0.7 | 3.710 |
| $NO_3$ + $NO_2$ (mg $l^{-1}$) | 0.4 + 0.1 | <0.01 + <0.1 |
| $NH_3$-N (mg $l^{-1}$) | 0.5 | 1.456 |
| TKN (mg $l^{-1}$) | 4.3 | 16.331[1] |
| $SiO_2$ (mg $l^{-1}$) | --- | 40 |
| Cl (mg $l^{-1}$) | 216 | 141 |
| $SO_4$-S (mg $l^{-1}$) | 52 | 261 |
| Na (mg $l^{-1}$) | 543 | 623 |
| Alkalinity (mg $CaCO_3$ $l^{-1}$) | 678 | 682 |
| Total Organic Carbon (mg $l^{-1}$) | 992 | 76[2] |

[1] value obtained from a sample collected on a different day (Nov. 7, 1985). Comparisons of the original TKN value to other data (unpublished data, MWQB) indicated that the original TKN value was abnormally low.

[2] estimated by summing DOC and POC.

phosphorus, and ammonia of the wastewater might have increased the metabolic rates of the riffle communities downstream of the kraft mill, but trends in the ambient concentrations of these inorganic nutrients (see Table 14.) and the consistently enhanced metabolic rates of the Flat Valley riffle site indicated that either the addition of kraft mill wastewater was not having a significant impact on riffle community metabolism downstream of the mixing zone or that the impact was being "masked" by elevated concentrations of nutrients due to a source upstream of the kraft mill.

Other Sources of Nutrients

Comparison of the water chemistry data among the riffle sites during August (see Table 14.) indicates that soluble reactive phosphorus and nitrate concentrations decreased from the upstream riffle sites to the downstream riffle sites. When these nutrient concentrations were compared to community metabolism variables, suspiciously high correlations were obtained between soluble reactive phosphorus concentrations and NCPP ($r = 0.71$), GPP ($r = 0.82$), and $R_{24}$ ($r = 0.93$) (Figure 7.). A similar relationship existed between nitrate concentrations and NCPP ($r = 0.60$), GPP ($r = 0.73$) and $R_{24}$ ($r = 0.88$)(Figure 8.). These correlations were not significant, however, possibly because of the limited amount of data available ($n=4$). (Note: when graphing and determining correlations between nitrate concentrations and the community metabolism variables, the detection limit (0.01 mg $NO_3$-N $l^{-1}$)

Table 14. Comparison of water chemistry variables determined during this study. Data are means of duplicate samples.

| Parameter | Date | Flat Valley | Harper's Bridge | Huson | Nine-mile |
|---|---|---|---|---|---|
| Turbidity (NTU) | Nov. | 0.61 | 0.65 | 0.83 | 0.80 |
| | Aug. | 1.9 | 2.3 | 3.1 | 3.6 |
| Hardness (mg $CaCO_3$ $l^{-1}$) | Nov. | 125 | 132 | 136 | 133 |
| | Aug. | 122 | 123 | 125 | 128 |
| Ca (mg $l^{-1}$) | Nov. | 35.2 | 36.9 | 38.0 | 37.3 |
| | Aug. | 33.5 | 33.5 | 34.2 | 35.1 |
| Mg (mg $l^{-1}$) | Nov. | 9.1 | 9.6 | 9.9 | 9.6 |
| | Aug. | 9.2 | 9.6 | 9.6 | 9.9 |
| $PO_4$-P (mg $l^{-1}$) | Nov. | 0.019 | 0.016 | 0.017 | 0.012 |
| | Aug. | 0.016 | 0.013 | 0.010 | 0.008 |
| TP (mg $l^{-1}$) | Nov. | 0.036 | 0.034 | 0.036 | 0.031 |
| | Aug. | 0.042 | 0.040 | 0.041 | 0.045 |
| $NO_3$-N* (mg $l^{-1}$) | Nov. | 0.05 | 0.05 | 0.05 | 0.04 |
| | Aug. | 0.06 | 0.05 | 0.02 | <0.01 |
| $NH_3$-N (mg $l^{-1}$) | Nov. | 0.011 | 0.012 | <0.005 | <0.005 |
| | Aug. | 0.010 | 0.010 | 0.009 | 0.006 |
| TKN (mg $l^{-1}$) | Nov. | 0.144 | 0.139 | 0.137 | 0.143 |
| | Aug. | 0.223 | 0.213 | 0.252 | 0.293 |
| $SiO_2$ (mg $l^{-1}$) | Nov. | 13.6 | 13.1 | 13.5 | 13.3 |
| | Aug. | 14.5 | 14.2 | 13.8 | 13.2 |
| Cl (mg $l^{-1}$) | Nov. | 2.2 | 2.4 | 3.3 | 3.2 |
| | Aug. | 2.1 | 2.3 | 2.8 | 2.8 |
| $SO_4$-S (mg $l^{-1}$) | Nov. | 8.94 | 9.74 | 10.24 | 10.26 |
| | Aug. | 5.54 | 5.65 | 6.25 | 6.20 |
| Na (mg $l^{-1}$) | Nov. | 7.3 | 7.3 | 10.4 | 9.9 |
| | Aug. | 6.7 | 6.7 | 8.5 | 8.4 |
| Alkalinity (mg $CaCO_3$ $l^{-1}$) | Nov. | 111 | 114 | 118 | 117 |
| | Aug. | 121 | 123 | 128 | 130 |
| DOC (mg $l^{-1}$) | Nov. | 1.1 | 1.5 | 1.4 | 1.4 |
| | Aug. | 2.8 | 2.2 | 2.4 | 2.3 |
| POC (mg $l^{-1}$) | Nov. | 0.4 | 0.3 | 0.4 | 0.5 |
| | Aug. | 0.7 | 0.8 | 1.1 | 1.2 |

* nitrite ($NO_2$) was always below the detection limit (<0.1 mg $NO_2$-N)

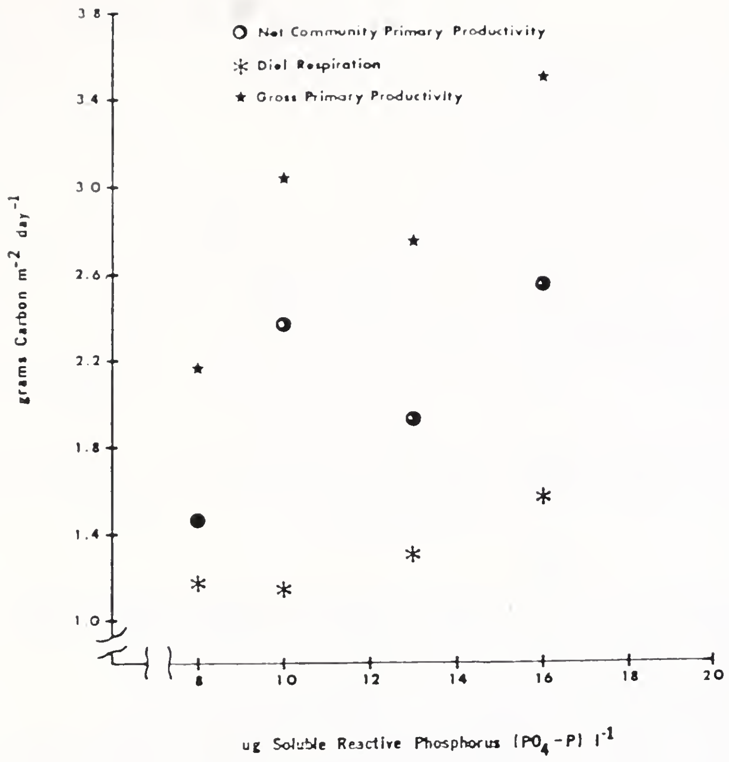

Figure 7. Comparison of soluble reactive phosphorus concentrations (ug PO$_4$-P l$^{-1}$) with metabolism variables (gr C m$^{-2}$ day$^{-1}$) measured during the August, 1985 synoptic studies.

was plotted for those data which were below the detection limit). These relationships implied that the enhanced metabolic rates observed at Flat Valley were due to elevated concentrations of soluble reactive phosphorus and nitrate; and, the low metabolic rates observed at Ninemile were due to correspondingly low concentrations of these inorganic nutrients.

Comparisons of the river Total Kjeldahl Nitrogen (TKN)

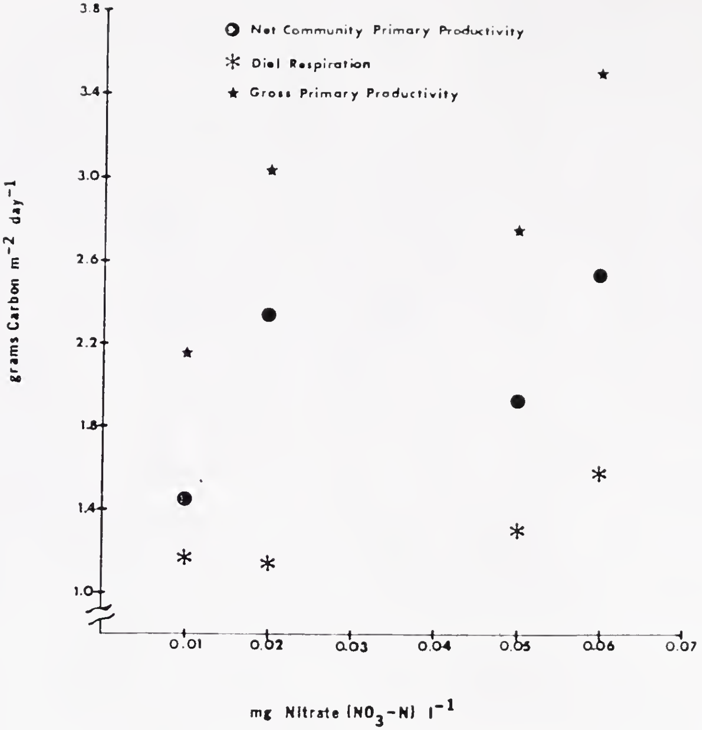

Figure 8. Comparison of nitrate concentrations (mg $NO_3$-N $l^{-1}$) with metabolism variables (gr C $m^{-2}$ $day^{-1}$) measured during the August, 1985, synoptic studies.

concentrations (an indicator of organic nutrients) (Table 14.) with the results of the synoptic studies (Table 3.) suggested no dominating relationships of TKN concentrations with riffle community metabolism. Indeed, during August the significantly ($p < 0.05$) reduced net community primary productivity of the Ninemile riffle community suggested that productivity was nutrient limited in spite of having the highest TKN concentration of all the riffle sites.

To assess what sources of nutrients might have been

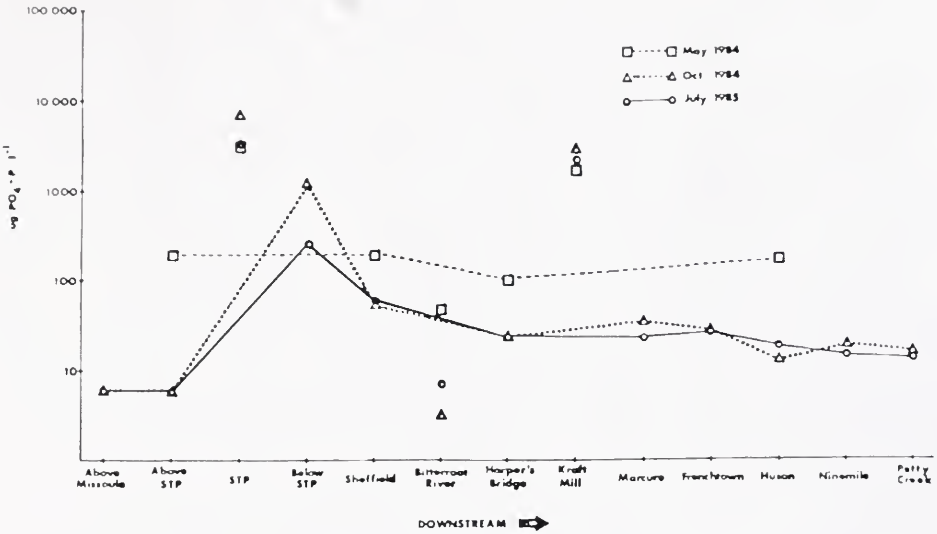

Figure 9. Downstream trends in soluble reactive phosphorus concentrations (ug $PO_4$-P $l^{-1}$) in the Clark Fork River--from the Clark Fork River above Missoula to the Petty Creek Fishing Access. Soluble reactive phosphorus concentrations of the wastewater from the Missoula sewage treatment plant (STP), the Bitterroot River, and the wastewater from the kraft mill are included. Data are from the Montana Water Quality Bureau (MWQB, unpubl.). Data are plotted on a logarithmic scale.

impacting riffle community metabolism of the Clark Fork River, the water quality data of this study was supplemented by water quality data taken on the Clark Fork River during 1984 and 1985 by the Montana Water Quality Bureau (unpublished data, MWQB).

In past studies (Spindler 1959; USEPA 1974), the Missoula sewage treatment plant was implicated as a major source of nutrients upstream of the kraft mill. Data collected during this study did indicate that the wastewater

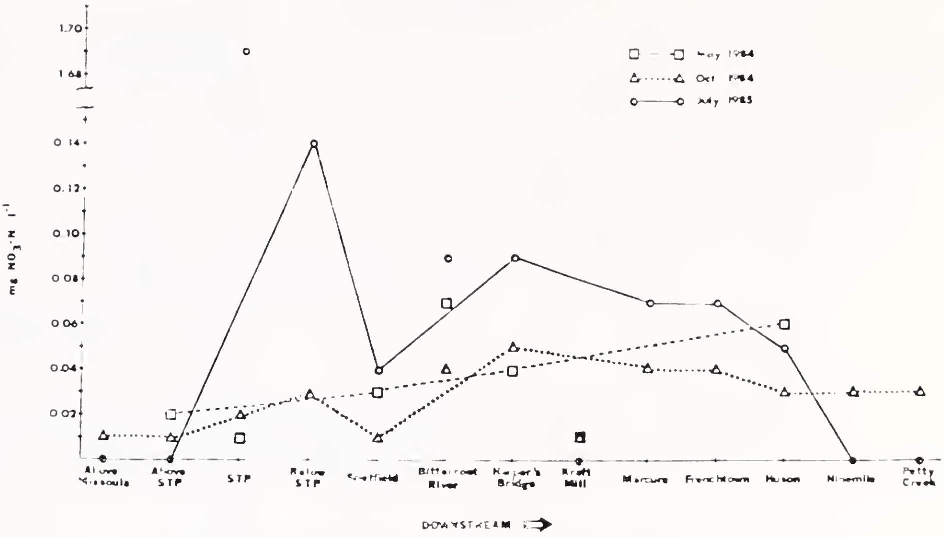

Figure 10. Downstream trends in nitrate concentrations (mg NO$_3$-N l$^{-1}$) in the Clark Fork River--from the Clark Fork River above Missoula to the Petty Creek Fishing Access. Nitrate concentrations of the wastewater from the Missoula sewage treatment (STP), the Bitterroot River, and the wastewater from the kraft mill are included. Data are from the Montana Water Quality Bureau (MWQB, unpubl.).

from the sewage treatment plant contained elevated concentrations of soluble reactive phosphorus (Figure 9.), nitrates (Figure 10.), and ammonia (Figure 11.). But a closer examination of the trends in soluble reactive phosphorus presented in Figure 9. indicated that during May the Clark Fork River above the sewage treatment plant had elevated concentrations of soluble reactive phosphorus from a nutrient source upstream of the sewage treatment plant. During the onset of the spring freshet, sediment-phosphorus

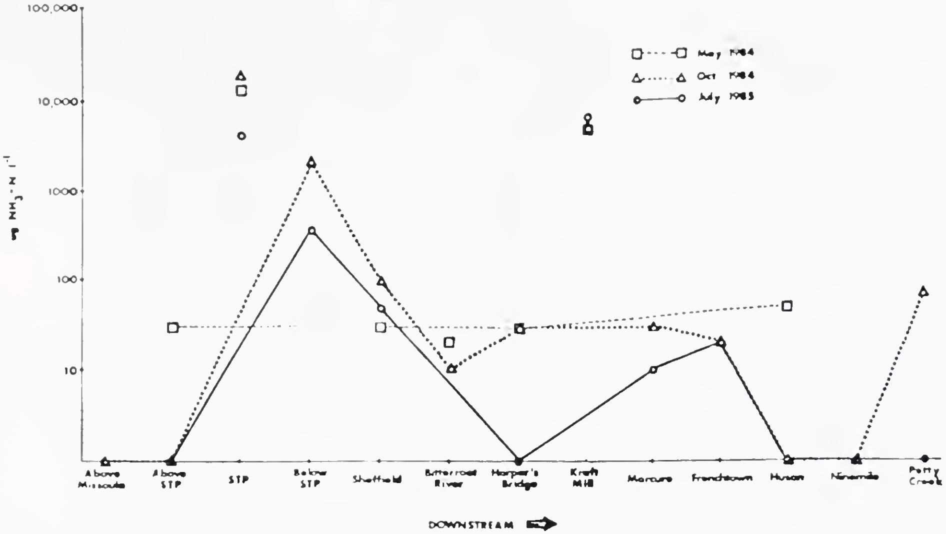

Figure 11. Downstream trends in ammonia concentrations (ug $NH_3$-N $l^{-1}$) in the Clark Fork River--from the Clark Fork River above Missoula to the Petty Creek Fishing Access. Ammonia concentrations of the wastewater from the Missoula sewage treatment plant (STP), the Bitterroot River, and the wastewater from the kraft mill are included. Data are from the Montana Water Quality Bureau (MWQB, unpubl.). Data are plotted on a logarithmic scale.

kinetics of the increased sediment load in the river probably caused the concentrations of soluble reactive phosphorus to also increase (Casey and Farr 1982; Logan 1982).

A closer examination of the nitrate trends (Figure 10.), revealed that the nitrate concentrations in the Clark Fork River increased below the confluence with the Bitterroot River, remained elevated throughout the Missoula Valley, but then decreased at the point where the river leaves the

Missoula Valley. Although mineralization of the elevated ammonia concentrations from the sewage treatment plant wastewater or the kraft mill wastewater might have kept these nitrate concentrations elevated throughout the study area, the elevated nitrate concentrations of the Bitterroot River suggested that other factors were involved. Based on descriptions of groundwater movement in the area, we hypothesized that inflowing groundwaters could contain enough nitrate to subsidize the nitrogen mass carried in the river channel of both the Clark Fork and the Bitterroot Rivers. To obtain more information about this possibility, we gathered a special set of samples for nitrate analyses at sites on the Clark Fork and Bitterroot Rivers above their confluence (Figure 1.) and at sites on the Clark Fork River downstream of the confluence (Figure 3.).

These nitrate data (Figure 12.) confirmed the contribution of nitrates to the Bitterroot and Clark Fork Rivers by groundwater. We found two groundwater seeps in the "backwaters" of the Bitterroot River at the Fort Missoula and the McClay Bridge sampling sites (Figure 1). Water samples taken from these seeps were found to have nitrate concentrations at least 10x the nitrate concentrations of the Bitterroot River (Figure 12.). These results supported earlier studies which, reported "elevated" nitrate concentrations for the groundwater under the city of Missoula (Juday and Keller 1973) and for the groundwater throughout the Missoula Valley (Newman 1981). The general groundwater

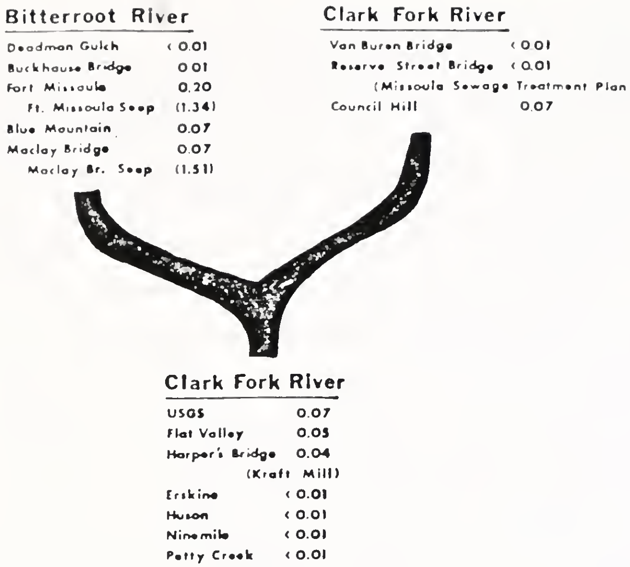

Figure 12. Downstream trends in nitrate concentrations (mg $NO_3$-N $l^{-1}$) measured during a special sampling run of the Bitterroot and Clark Fork Rivers on September 4, 1985. Site locations are given in Figures 1. and 3.

flows discussed earlier indicate that the Clark Fork River below Kelly Island also receives groundwater inputs of nitrate. Continuous nitrate inputs would keep the nitrate concentrations in the Clark Fork River elevated (as shown in Figure 12.) upstream of the kraft mill and upstream of Ninemile (as shown in Figure 10.). Since the morphology of the Missoula Valley constricts around the Clark Fork River between Huson and Ninemile, less groundwater might have been flowing into the river near Ninemile than might have been flowing into the river from the wider portions of the Missoula Valley. Less groundwater flow would have decreased the nitrate contributions to the river from groundwater. With reduced nitrate contributions from groundwater, the nitrate in the river would be rapidly taken up by the river periphyton; nitrate concentrations in the river at this point would be expected to decline. Such a decline in nitrate concentrations was measured in August, 1985 (see Table 14.).

These results suggested that groundwater flow into the river may be an important factor in determining metabolic rates as well as the general water quality of the Clark Fork River. If groundwater flow into the river was significant in the Missoula Valley, then impacts from point sources could be reduced by dilution processes. On the other hand, polluted groundwater (e.g. seepage from septic sytems or buried gasoline tanks) could result in water quality degradation of the Clark Fork River.

To compare the relative importance of the various inorganic nutrient sources to the Clark Fork River on an equal basis, the loading rates of soluble reactive phosphorus and inorganic nitrogen (nitrate + ammonia) by the Clark Fork River above the sewage treatment plant, the Missoula sewage treatment plant, the Bitterroot River, and the kraft mill were determined from the 1984 and 1985 water quality data of the Montana Water Quality Bureau (unpublished data, MWQB). Groundwater contributions of inorganic nutrients were not included because information was not available to estimate the seasonal qualities and quantities of groundwater flows to the river.

Table 15. Loading rates (gr P $sec^{-1}$) of soluble reactive phosphorus to the Clark Fork River from selected nutrient sources. STP is the Missoula sewage treatment plant.

| Date | Clark Fork River Above STP | STP | Bitterroot River | Kraft Mill |
|---|---|---|---|---|
| May 1984 | 63.5 | 1.0 | 13.0 | 3.2 |
| Oct. 1984 | 0.3 | 2.5 | 0.2 | 0.5 |
| July 1985 | 0.2 | 1.2 | 0.1 | 0.0 |

Table 16. Loading rates (gr N $sec^{-1}$) of inorganic nitrogen (nitrate + ammonia) to the Clark Fork River from selected nutrient sources. STP is the Missoula sewage treatment plant.

| Date | Clark Fork River Above STP | STP | Bitterroot River | Kraft Mill |
|---|---|---|---|---|
| May 1984 | 16.7 | 4.4 | 24.5 | 9.1 |
| Oct. 1984 | 0.5 | 5.4 | 1.9 | 0.8 |
| Aug. 1985 | 0.0 | 2.1 | 0.9 | 0.0 |

During the spring freshet, the upstream sources of soluble reactive phosphorus in the Clark Fork River contributed a phenomenal amount of phosphorus to the Missoula Valley (Table 15). The Bitterroot River also contributed a substantial amount of soluble reactive phosphorus to the Clark Fork River. During other times of the year when the river flows were less, however, the Missoula sewage treatment plant dominated the contributions of soluble reactive phosphorus to the Clark Fork River.

Analysis of the inorganic nitrogen (nitrate + ammonia) loadings from the various sources again indicated dominant nitrogen contributions of the Clark Fork and Bitterroot Rivers during the spring freshet (Table 16.). During low flows, the Missoula sewage treatment plant and the Bitterroot River contributed most of the inorganic nitrogen to the Clark Fork River.

## Experimental Program: Effects of Diluted Kraft Mill Wastewater on Benthic Community Metabolism

Previous studies found many toxic substances in pulp and paper mill wastewaters including resin acids, fatty acids, terpenes, pyrene, fluoranthene, and/or chlorinated hydrocarbons (Kelso et al. 1977; Moore and Love 1977; Kinae et al. 1981; Leung and Sell 1982). Moore and Love (1977) found that a solution containing 1.0% kraft mill wastewater reduced algal productivity mainly due to the presence of dehydroabietic acid, a resin acid.

Although dehydroabietic acid was also found in the wastewater of the Champion International kraft mill (USEPA 1985), the results of preliminary experiments with the kraft mill wastewater indicated that a 50% concentration of kraft mill wastewater was required to reduce net community primary productivity. The wastewater used by Moore and Love (1977) was subjected only to primary treatment whereas the wastewater from the Champion International kraft mill was subjected to secondary treatment and a minimum holding time of 10 days before being discharged into the Clark Fork River (Shewman et al. 1984). Rainville (1975) found that the toxicity of pulp and paper mill wastewater was reduced by aeration or storage. In addition, some recent studies were completed showing that secondary treatment reduced the toxicity and mutagenicity of pulp mill wastewaters (Nestmann et al. 1984; Leuenberger et al. 1985), although Leuenberger et al. (1985) also found that chlorinated compounds were only partly eliminated by the activated sludge process. (The pulp bleaching process was probably the source of these chlorinated compounds (Leung and Sell 1982; Karma et al. 1983)) Therefore, the toxicity of the unbleached kraft mill wastewater from Champion International was probably reduced due to secondary treatment.

The observed presence of algae (both phytoplankton and periphyton) and zooplankton in the wastewater holding ponds also implied that the wastewater toxicity was reduced. In addition to the reduction of toxicity, secondary treatment of the kraft mill wastewater might cause other changes in the wastewater quality (Table 13.) from the wastewater charactersitics previously described (MDHES 1974).

Per~~haps~~ the most surprising result of this study is the fact that the kraft mill wastewater had the capability for photosynthesis. This photosynthesis was primarily due to photosynthetic bacteria although some algae were observed in the wastewater ponds. Two genera of these photosynthetic bacteria were identified as *Chlorobium* and *Rhodopseudomonas* (McNeil, UMBS, pers. comm.) from samples of wastewater taken to the Biological Station. As an additional surprise, the kraft mill wastewater , *sampled from the same location throughout a 24 hour period during the summer*, could unpredictably change its metabolism characteristics within that 24 hour period. This change in metabolism characteristics was apparently due to the abundance of the photosynthetic bacteria. When the photosynthetic bacteria were abundant in the wastewater, the wastewater had a "greenish tinge" in color. When the photosynthetic bacteria were scarce, the wastewater had a "brown" color.

The results of the *in situ* experiment (Table 17.) indicated that the primary productivity measurements had variances dependent upon the means; consequently, these data were transformed logarithmically before determining tests of significance. The significant ($p < 0.001$) reduction in net community primary productivity could have been due to three factors: 1) the wastewater color decreasing the light intensity within the chamber, 2) the concentration of toxic

Table 17. Comparison of metabolism variables measured during the *in situ* chamber experiment using a treatment of a 1:1 mixture of kraft mill wastewater and Clark Fork River water. Experiment was conducted on September 25, 1985. Data are means.

| Parameter | River Water (Control) | 1:1 Mixture (Treatment) |
|---|---|---|
| Net Community Primary Productivity ($mg\ C\ m^{-2}\ day^{-1}$) | 1630 | 420*** |
| Diel Respiration ($mg\ C\ m^{-2}\ day^{-1}$) | 910 | 1190ns |
| Gross Primary Productivity ($mg\ C\ m^{-2}\ day^{-1}$) | 2100 | 1030* |
| Net Daily Metabolism ($mg\ C\ m^{-2}\ day^{-1}$) | +1190 | - 160 |
| P:R[1] | 2.31 | 0.87 |

*** $p < 0.001$

* $p < 0.05$

ns not significant ($p > 0.05$)

[1] Gross Primary Productivity/Diel Respiration

substances in the wastewater or 3) the increased salinity of the wastewater.

Respiration measurements did not require transformation of the data before determining tests of significance. The treated chambers did not have significantly ($p > 0.05$) different respiration rates from that of the control chambers. These results implied either 1) the respiration rate (including the decomposition rate) of the 1:1 mixture of kraft mill wastewater to river water was negligible when compared to the benthic respiration of the Clark Fork River, or 2) the toxicity of the wastewater, which would have decreased respiration, was compensated by the additional respiration from the organic matter in the kraft mill wastewater.

Perhaps the greatest acute impact of the kraft mill wastewater on riffle community metabolism was exemplified by comparing the net daily metabolism values and the P:R ratios of the control chambers to those treated with a 1:1 mixture of kraft mill wastewater and river water. The treated chambers experienced heterotrophic conditions whereas the control chambers experienced autotrophic conditions. The heterotrophic conditions, caused by the addition of kraft mill wastewater, eventually would have caused the community structure of the impacted riffle community to change.

## Experimental Program: Effect of Diluted Kraft Mill Wastewaters on Water Column (vs Benthic) Metabolism

Water column metabolism and changes in water column metabolism due to the addition of kraft mill wastewater (Table 18.) were negligible when compared to benthic

Table 18. Comparison of metabolism variables measured during the water column metabolism experiment. River water for the mixtures (parts kraft mill wastewater: parts Clark Fork River water) were obtained at the Petty Creek Fishing Access. Experiment was conducted on September 20, 1985. Data are based on 3-hour incubation periods.

| Parameter | Composition of Solutions Used for Incubations | | | | |
|---|---|---|---|---|---|
| | River Water | 1:200 | 1:20 | 1:1 (Brown) | 1:1 (Green) |
| Net Community Primary Productivity (mg C $m^{-2}$ day$^{-1}$) | 0.0 | 0.2* | 0.5* | 3.2* | 3.2* |
| Diel Respiration (mg C $m^{-2}$ day$^{-1}$) | 0.0 | 0.0 | 0.5 | 1.3 | 4.7 |
| Gross Primary Productivity (mg C $m^{-2}$ day$^{-1}$) | 0.0 | 0.2* | 0.8* | 3.9* | 5.8* |

* value determined from the Net Community Primary Productivity of both "green" and "brown" wastewater.

community metabolism of the Clark Fork River (Table 3.). "Brown" wastewater was used during most of this study. If "green" wastewater had been used more frequently during this study, the changes in water column metabolism due to the addition of kraft mill wastewater might have been important. Since there was no known method of "controlling" the quality (brown vs. green) of wastewater obtained from the same location in the holding ponds, the experimental work was conducted on both green and brown wastewater, as available from the holding ponds.

No net community primary productivity or respiration was detected (Table 18.) in the Clark Fork River water collected at the Petty Creek site. The low metabolic rates observed at the Petty Creek site were similar to the light-dark bottle incubation results from the other riffle sites (Flat Valley, Harper's Bridge, Huson, and Ninemile).

No diel respiration was detected for the 1:200 mixture of kraft mill wastewater and river water. The diel respiration of the 1:20 mixture of kraft mill wastewater and river water was barely detectable. The respiration rate increased between the 1:20 mixture and the 1:1 mixture of kraft mill wastewater and river water indicating that the respiration rate was dependent upon the wastewater concentration. The difference in respiration rates between the brown and green wastewaters for the 1:1 mixture of kraft mill wastewater (Table 18.) indicated that the quality of the wastewater was important to respiration rates, although no difference in respiration was detected in the 1:20 mixture between green and brown wastewaters. Comparison of the benthic chamber experimental results (see Table 17.) with the water column metabolism experimental results (Table 18.) indicated that the respiration rate of the organic matter in the 1:1 mixture of kraft mill wastewater to river water was negligible when compared to the respiration of the benthos.

When determining the net community primary productivity of the mixtures of kraft mill wastewater and river water, the positive increases of dissolved oxygen concentrations due to the green effluent and to the brown effluent were summed together. The primary productivity measurements might have been underestimated because the metabolism measurements from the first three hours of the decomposition study were not included in the primary productivity calculations. These measurements were not included because technical problems, which were immediately resolved, provided invalid results for the first data set. As the concentration of kraft mill wastewater increased, the net community primary productivity increased (Table 18.). The green effluent had a higher net community primary productivity rate than the brown wastewater (Table 19.). Even in the 1:200 mixture of kraft mill wastewater and river water, primary productivity was detected. This last result suggested that it might be possible for the bacteria in the kraft mill wastewater to produce organic matter by photosynthetic processes, even after the wastewater was discharged into the river. Since no water column primary productivity was detected at the riffle sites downstream of the kraft mill, this instream bacterial photosynthesis, if it occurred at all, appeared to be limited to the mixing zone.

Data from the August water chemistry samples indicated that the particulate organic carbon concentrations were higher at the riffle sites downstream of the kraft mill than the concentrations at the riffle sites upstream of the mill; however, the kraft mill was not direct discharging its effluent during this period. These samples were collected a day after the first major thunderstorm passed through the area, following a two month drought. The resulting spate might have resuspended organic matter that settled in the mixing zone downstream of the kraft mill or increased sloughing of periphyton from the river bottom (cf. Stockner and Shortreed 1978). Therefore, the increased particulate organic carbon concentrations observed at the downstream riffle sites during the spate could have been organic matter from algal biomass which had been sloughed off the river

Table 19. Changes in dissolved oxygen concentrations of the 1:1 mixture of kraft mill wastewater and Clark Fork River water obtained at Petty Creek Fishing Access during the water column metabolism experiment. Experiment was conducted on September 20, 1985. Wastewater quality is also included.

| Time | Light Bottle (mg $O_2$ $l^{-1}$) | Dark Bottle (mg $O_2$ $l^{-1}$) | Effluent Quality |
|---|---|---|---|
| 8:40-11:15 | +0.6 | -0.6 | Brown |
| 10:55-14:10 | +1.0 | -0.4 | Brown |
| 13:45-17:00 | +1.7 | -0.5 | Brown |
| 16:45-19:50 | +5.9 | -2.1 | Green |
| 19:35-22:45 | -1.0 | -1.4 | Green |
| 22:30- 2:05 | -0.3 | -0.4 | Brown |
| 1:40- 5:00 | -0.4 | -0.4 | Brown |
| 4:40- 7:35 | -1.4 | -1.4 | Green |

bottom, from the kraft mill wastewater (see Appendix B.), or organic matter from other sources in the Missoula Valley which accumulated in the kraft mill wastewater mixing zone.

Water samples for some of the mixtures of kraft mill wastewater and Clark Fork River water were analyzed for water chemistry variables (see Table 20.). The 1:200 mixture had characteristics very similar to the river water. The 1:1 mixture had characteristics more similar to the full strength

Table 20. Comparison of water chemistry variables among mixtures of kraft mill wastewater and Clark Fork River water taken from the Petty Creek Fishing Access. Data are means of duplicate samples on collected September 3, 1985.

| Variable | 1:1 | 1:200 | River Water |
|---|---|---|---|
| Turbidity (NTU) | 20 | 2.0 | 0.83 |
| Hardness (mg $CaCO_3$ $l^{-1}$) | 171 | 133 | 135 |
| Ca (mg $l^{-1}$) | 47.9 | 36.6 | 37.0 |
| Mg (mg $l^{-1}$) | 12.6 | 10.2 | 10.3 |
| $PO_4$-P (mg $l^{-1}$) | 0.145 | 0.004 | 0.008 |
| TP (mg $l^{-1}$) | 1.806 | 0.050 | 0.031 |
| $NO_3$-N[1] (mg $l^{-1}$) | <0.01 | <0.01 | <0.01 |
| $NH_3$-N (mg $l^{-1}$) | 1.017 | <0.005 | 0.006 |
| TKN (mg $l^{-1}$) | 7.896[2] | 0.364 | 0.221 |
| $SiO_2$ (mg $l^{-1}$) | 22.0 | 11.7 | 10.2 |
| Cl (mg $l^{-1}$) | 73.8 | 4.2 | 3.5 |
| $SO_4$-S (mg $l^{-1}$) | 139.77 | 9.12 | 7.90 |
| Na (mg $l^{-1}$) | 295.4 | 12.5 | 9.4 |
| Alkalinity (mg $CaCO_3$ $l^{-1}$) | 406 | 133 | 129 |
| DOC (mg $l^{-1}$) | 30.9 | 2.7 | 1.7 |
| POC (mg $l^{-1}$) | 13.1 | 1.5 | 0.8 |

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[1] nitrite below detection limit ($< 0.1$ mg $NO_2$-N $l^{-1}$).

[2] value obtained from a different sample (Nov. 7, 1985).

wastewater. One characteristic common to all the samples was the very low nitrate concentrations. Bacterial production might have been nitrate limited so that the observed respiration (including decomposition) rates were less than they might be (Howard 1985) during other times of the year.

Other factors which might effect decomposition rates include availability of organic nutrients, total suspended solid concentrations, location, and time of year (Bartholomew and Pfaender 1983; Cummins et al. 1983; Wang et al. 1984; Howard 1985).

The changes in diel respiration between green and brown wastewater (Table 18.); and the existence of primary productivity in the kraft mill effluent refuted the assumption that respiration was solely due to decomposition of the organic matter in the kraft mill wastewater. Therefore, the diel respiration rates given in Table 18. cannot be used directly as decomposition rates.

# CONCLUSIONS

## Seasonal Variations of Riffle Community Metabolism

The riffle community metabolism data indicate that the trophic conditions of the Clark Fork River changed drastically with season. Cold temperatures and shorter daylight periods during November limited photosynthesis in the river. Therefore, respiration dominated, as surplus organic matter derived from late summer algal production and allochthonous inputs were catabolized (consumed) by stream organisms. Consequently, P:R ratios were less than 1.0.

Spring, on the other hand, was a time of growth. The warmer temperatures and longer daylight periods supported a high rate of primary productivity. Rocks which were recently inundated by the river were quickly colonized and covered with algae. Higher primary production increased the P:R ratios above 1.0.

During the summer, the higher temperatures supported an even higher rate of primary productivity and respiration as long as nutrients were available. Primary productivity and respiration in the Clark Fork River appeared to be nitrate-limited during the summer, except in those areas (e.g. Clark Fork River between its confluence with the Bitterroot River and Huson) where groundwater apparently provided a nitrate subsidy. In those areas receiving nitrate-rich groundwaters, primary productivity and respiration were probably phosphorus-limited. The high summer respiration of the benthic communities and the low solubility of oxygen in river water, due to high summer temperatures, indicated that the dissolved oxygen concentrations of the Clark Fork River could decrease to the minimum water quality standard of 7.0 ppm. (and possibly even decrease below this standard) quite often during the summer.

Productivity of the river below Missoula appeared to be enhanced as a result of nutrient inputs from the sewage treatment plant, located upstream of the kraft mill, and nitrate inputs from the Bitterroot River and nonpoint groundwater sources.

## Impact of the Kraft Mill on the Clark Fork River

We were unable to distinguish an impact on riffle community metabolism from the kraft mill due to the very high ambient productivity of the river. The elevated phosphorus and ammonia concentrations of the kraft mill wastewater might have enhanced productivity in the study area, but this impact was "masked" by the high production potential mediated by waters flowing into the kraft mill discharge area.

Experimental studies indicated that a 50% concentration of "brown" kraft mill wastewater reduced net community primary productivity of the riffle communities in the Clark Fork River. This decrease in net community primary productivity was probably due to: 1) the color of the kraft mill wastewater reducing the light intensity in the metabolism chambers, 2) the concentrations of residual toxic substances in the wastewater, or 3) the increased salinity of the wastewater.

The water column metabolism studies revealed that the kraft mill wastewater often contained a photosynthetic bacterial community, which may drastically alter the metabolic characteristics of the wastewater within short time periods. More studies are required to understand the dynamic nature of this biological community.

The kraft mill was just one of many point and nonpoint sources of nutrients and organic matter in the Clark Fork River watershed. The enhanced productivity and respiration observed in the Clark Fork River resulted from the cumulative effects of these various point and nonpoint disturbances in the watershed.

## Riffle Community Metabolism as a Measure of Water Quality

The results of this study indicate that riffle community metabolism can be used to detect water quality degradation. The enhanced metabolic rates measured upstream of the kraft mill were probably related to the enhanced concentrations of inorganic nutrients in the river due to upstream sources. The metabolism study also allowed resolution of groundwater nitrate subsidies to this reach of the Clark Fork River.

Although traditional water quality indicators could have been used with less time, money, and effort expended than measuring metabolism required, traditional indicators only address the material aspects of an environmental impact and tend to ignore the energy aspects. Riffle community metabolism complements the traditional water quality indicators by addressing the energy aspects of an environmental impact under the environmental conditions during which the impact occurs. Hence, when comparing changes in metabolism rates with corresponding changes in the traditional water quality indicators, insights are provided to how an impact by a "pollution source" occurs in the environment rather than just detecting the presence of an impact.

The use of riffle community metabolism for environmental impact assessment, however, could be much improved over its use in this study. Because riffle community metabolism is sensitive to environmental changes, metabolism measurements should be recorded simultaneously upstream and downstream from a suspected pollution source. To separate the water column metabolism from the benthic metabolism, light-dark bottle incubations or metabolism measurements of a chamber containing only river water should be run simultaneously with chambers containing benthos. Since river conditions continually change, both benthic and water column metabolism should be determined seasonally, if not more frequently. Water samples for chemical analyses should be collected on the same day that the metabolism data is recorded. Integrating these changes into the riffle community metabolism measurements could reduce the variance of the metabolism values so that the interactions among the various water quality variables could be discerned more easily.

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# APPENDIX A.

## What is Community Metabolism?

A river is a living community. The organisms (i.e. the algae, fish, insects, microorganisms, etc.) that exist in the river need energy to live, grow, and reproduce. The organisms obtain energy by consuming food in the form of organic matter.

The food for stream organisms comes from two main sources: 1) algae and other aquatic plants produce food by instream photosynthesis (known as autochthonous inputs of energy); and 2) organic matter which is produced on land and which certain stream organisms can consume (known as allochthonous inputs of energy). The amount and proportion of organic matter contributed to a river food chain from these main sources differ for different streams. Allochthonous inputs of energy dominate the energy budget of many streams draining the deciduous forests of the eastern United States (Hall 1972; Fisher and Likens 1973; Cummins 1974; Hornick et. al. 1981; Hill and Webster 1982). In studies of streams draining the drier western United States, however, autochthonous inputs of energy dominate the streams' energy budgets (Minshall 1978; Busch and Fisher 1981; Cushing and Wolf 1984). Hence, in this and many other ways, the characteristics of a river or stream are dependent upon the characteristics of the watershed that it drains (Hynes, 1975). The absolute and relative contributions of allochthonous and autochthonous energy inputs may even change between different reaches of the same river system (Hall 1972; Minshall et. al. 1983: Naiman 1983; Stanford and Ward 1983; Bott et. al. 1985; Minshall et. al. 1985) and may change seasonally for the same reach of a river system (Hall 1972; Naiman 1983; Bott et. al. 1985).

Another important consideration about the availability of organic matter to stream organisms is the "quality", especially as food, of the organic matter. Some types of organic matter have a higher nutritive value to stream organisms than other types of organic matter in the same way that a T-bone steak has a higher nutritive value than the wood cambium of a Ponderosa Pine to humans. Organic matter that has a low nutritive value to stream organisms is referred to as refractory organic matter and that which has a high nutritive value and can be readily assimilated by stream organisms is referred to as labile organic matter. Some studies (Hornick et. al. 1981; Hill and Webster 1982) have suggested that autochthonous inputs of organic matter tend to have a higher food quality to stream organisms than allochthonous inputs of organic matter.

The different contributions of autochthonous food and and allochthonous food to the consumers of a river or stream suggest that the types and abundances of stream organisms (collectively called community structure by ecologists) and the interactions among these organisms (stream ecology) may be quite different for various river systems (Cushing et. al.

1983) and may even be different from one section of a particular river system to another only a kilometer away (Vannote et. al. 1980). Hence, a disturbance to a community dependent upon allochthonous inputs of energy may have different consequences in a community dependent upon autochthonous inputs of energy.

A river community may be subjected to a variety of disturbances. Some of these disturbances are "natural" : spring runoff, runoff from storm events (Wallace et. al. 1982; Casey and Farr 1982; Verhoff et. al. 1982), wildfires (Tiedemann et. al. 1978), or even large scale pest epidemics (Potts 1984). Other disturbances result from human activites including agriculture (Logan 1982; Peterjohn and Correll 1984; Dorich et. al. 1984), logging (Likens et. al. 1970; Meyer and Tate 1983; Webster et. al. 1983), mining (Wieder and Lang 1984), dam construction (Ward and Stanford 1979, 1982; Hauer and Stanford 1982), or the development of urban areas (Smart et. al. 1985).

These disturbances can influence the absolute and relative contributions of allochthonous and autochthonous inputs of energy to a river or stream, and can also influence the resulting food quality of these energy sources. The addition of nutrients (phosphorus, nitrate, ammonia, etc.) can increase the autochthonous resource of energy by supporting a higher rate of photosynthesis by algae and other aquatic plants (Stockner and Shortreed 1978; Elwood et. al. 1981; Horner and Welch 1981). Conversely, the addition of toxic substances to a river may decrease the autochthonous inputs of energy by inhibiting photosynthesis (Moore and Love 1977; Lewis and Gerking 1979; Leland and Carter 1985). The anthropocentric additions of organic matter are simply allochthonous sources of energy to stream organisms (cf. Warren et. al. 1964).

To assess the impact of a particular human activity on a river system, the absolute and relative contributions of allochthonous and autochthonous energy inputs, both naturally and as effected by human activity, to the affected river need to be estimated. The principal techniques for analyzing the importance of the two main sources of food to stream organisms is to measure the metabolism of the river community.

Community metabolism is the generic term for energy fixation and use by a biological community. Most commonly, it is measured by the production of oxygen in the stream due to photosynthesis of the aquatic plants (a measure of autochthonous inputs of energy) and the consumption of oxygen due to the respiration of stream organisms and the decay of organic matter in the stream (a measure of the total consumption of all energy by the stream consumers, including the consumption of allochthonous energy). The amount of organic matter produced or consumed can be determined approximately from the changes in dissolved oxygen concentrations by using the stoichiometric equations in Table A-1.

When stream organisms process food for their own energy and material requirements, they use the oxygen dissolved in

Table A-1. Generalized relationship between carbon and oxygen in photosynthesis and respiration (Odum 1971).

Respiration

$CH_2O + O_2 \longrightarrow CO_2 + H_2O + \text{energy}$

(food)

Photosynthesis

$CO_2 + H_2O + \text{energy} \longrightarrow CH_2O + O_2$

where: $CH_2O$ = organic matter

$O_2$ = oxygen

$CO_2$ = carbon dioxide

$H_2O$ = water

the river. This consumption of oxygen is known as respiration. Respiration includes the processes of both assimilation and decomposition. All stream organisms (including algae and aquatic plants) respire 24 hours a day. During the night, the respiration of virtually all stream organisms causes the dissolved oxygen of the river water to decrease. The amount of organic matter consumed during respiration can be estimated from the night-time decreases of dissolved oxygen (Odum 1956).

During the day, photosynthesis by algae and other aquatic plants produces free oxygen and converts carbon dioxide to organic matter. If, at any point in time, the photosynthetic rate of the algae and aquatic plants is greater than the respiration rate of the stream organisms, then the dissolved oxygen concentration and organic matter in the river will increase. The net gain in organic matter is known as net community primary productivity (NCPP). Net community primary productivity is determined from the positive day-time changes of dissolved oxygen in the river (Odum 1956).

Gross primary productivity (GPP) measures how much organic matter would be produced by photosynthesis, if respiration were not occurring during the day. It is calculated by adding the net community primary production to the respiration that occurs during the photoperiod (Naiman 1983).

Net daily metabolism and the ratio of production/respiration (P:R) are community metabolism variables which determine the relative importance of the two main food sources to stream organisms. Net daily metabolism is calculated by subtracting the amount of respiration which occurs over a 24 hour period (known as diel respiration) from the gross primary productivity of that same 24 hour period. The P:R ratio is calculated by dividing the gross community primary productivity by the diel respiration.

If the net daily metabolism is positive or the P:R ratio is greater than 1.0, then photosynthesis by algae provides a dominant food source and the community is considered autotrophic. If the net daily metabolism is negative or the P:R ratio is less than 1.0, then the stream organisms are converting more organic matter into energy than algal photosynthesis can provide; and, in this scenario the community is considered heterotrophic. Under heterotrophic conditions, the organic matter being consumed is either "surplus" organic matter produced by algal photosynthesis during other times of the year or it may be from allochthonous inputs of organic matter.

There are several methods for measuring community metabolism (Hall and Moll 1975; Bott et. al. 1978). In the open water (or "free water") techniques, water samples are collected from the stream at regular intervals for a 24 hour period. These samples are analyzed for either dissolved oxygen concentrations (Odum 1956; McDiffett et. al. 1972) or dissolved carbon dioxide concentrations (Wright and Mills 1967). The diurnal changes in dissolved oxygen (or carbon dioxide) concentrations are then used to calculate metabolism as described above in Table A-1. except the influence of groundwater inputs and gas diffusion on the dissolved oxygen concentration must be considered and corrected for. In turbulent streams, the determination of a gas exchange coefficient may be difficult and/or the correction for gas diffusion may be greater than the metabolic activity being measured (Bott et. al. 1978).

These problems are circumvented with the use of chambers or light-dark incubation bottles for estimating benthic and water column metabolism respectively. Since the changes of dissolved oxygen (or carbon dioxide) concentrations within the chambers or incubation bottles are due only to the metabolic activity of the enclosed community, estimates of groundwater inputs or gas diffusion are not required for calculating the community metabolism variables. Unfortunately, container effects may occur such that the environment influencing the community metabolism within the chamber is different from the "real" environment (Kowalczewski and Lack 1971; Rogers et. al. 1978; Jeppesen 1982; Nowell and Jumars 1984). We believe these container effects would be negligible when using chambers to determine community metabolism as a measure of water quality degradation.

However, since rivers are spatially very heterogeneous, measurements of community metabolism would require many chambers (Bott et al. 1978). Furthermore, to detect impacts of kraft mill effluent would require even more chambers due to the statistical needs of replication. The logistics of operating so many chambers and the difficulty of obtaining material from certain areas of the river (e.g. pools) made determination of community metabolism for the total river community impractical. Because of these difficulties, efforts were concentrated on determining the metabolism of the river's riffle communities as a measure of water quality degradation.

The riffle communities were chosen as study sites because these communities are the portion of the river where autotrophic productivity occurs (Margalef 1965) and because these sites are more accessible than other parts of the river. If the kraft mill effluent contained nutrients, then the net community primary productivity of the riffle communities were expected to increase. If addition of organic matter from the kraft mill caused a significant impact on the river, decomposers like "sewage fungus" were expected to develop in the riffle communities which would cause respiration to dominate primary productivity in these communities (Boyle and Scott 1984).

# APPENDIX B.

## Organic Matter and Other Water Chemistry Variables

From the water samples taken during November and August, turbidity, chloride, sulfate, sodium, and alkalinity were found in greater concentrations at the riffle sites downstream of the kraft mill than the riffle sites upstream of the kraft mill (see Table 14.). Large concentrations of these variables were found in the kraft mill wastewater (see Table 13.) so the increased concentrations of these variables in the Clark Fork River downstream of the kraft mill might have been due to the addition of kraft mill wastewater to the river. This interpretation should be made cautiously because turbidity, sulfate, and alkalinity changed seasonally at all four riffle sites, indicating that other factors were present influencing the values obtained for these variables. Sodium and chloride did not experience these seasonal changes at all four riffle sites. The sodium and chloride concentrations of the downstream site did not increase as much during August as during November. This "seasonal" difference was probably due to the direct discharge program of the kraft mill. The kraft mill was not direct discharging wastewater when the August water chemistry samples were collected, but the kraft mill was direct discharging wastewater when the November water chemistry samples were collected. The increase of sodium and chloride concentrations at the riffle sites downstream of the kraft mill during August was probably due to groundwater seepage of kraft mill wastewater. The introduction of the wastewater's elevated sodium and chloride concentrations to the river might have affected the organic carbon dynamics of the Clark Fork River.

The dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations of the river water increased at all riffle sites from November to August. The DOC concentrations were the same among sites during November and August (see Table 14.). The POC concentrations were the same among the riffle sites during November, but during August, the POC concentrations were greater at the riffle areas downstream of the kraft mill than the upstream riffle sites. The increased POC concentrations might have been due to enhanced photosynthesis in the mixing zone which resulted from the addition of nutrients from the kraft mill or might have been directly due to the addition of organic matter in the kraft mill wastewater.

Recent macroinvertebrate (mainly stream insects) studies in the Clark Fork River by the Institute of Paper Chemistry (Rades 1985) suggested that increases in filter-feeding caddisflies (Hydropsyche) immediately downstream of the kraft mill were probably a result of introducing kraft mill wastewater into the Clark Fork River, but before 1984 no wastewater was directly discharged into the river during the summers. The increased abundance of caddisflies was limited to those areas of the river influenced by the upwelling of wastewater in groundwater seepage from the rapid infiltration basins (Rades 1985).

Filter feeders are not believed to feed directly on dissolved organic carbon. Instead, it is thought that DOC is converted to POC before the organic matter can be consumed by the filter feeders (Lush and Hynes 1978). The mechanisms for the formation of POC from DOC include: 1) changes in the physico-chemical properties of river water such as changes in pH, calcium ion concentration (i.e. hardness), salinity, and turbulence (Lush and Hynes 1973, 1978; Wallace and Merritt 1980; Mulholland 1981; Jensen and Sondergaard 1982; Krueger and Waters 1983); 2) adsorption onto specific clay mine: amorphous solid phases of hydrous aluminum and iron oxides, and fine particulate matter (Dahm 1981); and 3) the scavenging of bacteria, dissolved organic matter, and other microfines by bubbles--produced either by the metabolism of aquatic plants and decomposers, or generated at the surface of the river by turbulence (Wallace and Duce 1978; Norhrans 1980; Durako et al. 1982; Weber et al. 1983; Wotton 1984).

Since the kraft mill wastewater had greater salinity and hardness than the Clark Fork River, the concentration gradient to the lower hardness and salinity of the river could have caused the formation of POC from the DOC of the river, or from the DOC of the wastewater as the wastewater seeped into the river. The kraft mill wastewater was also found to contain high concentrations of iron (unpubl. data of the Montana Water Quality Bureau) and aluminum (USEPA 1985). If these metals formed oxides, the DOC could have adsorbed onto these oxides and formed particulate organic carbon.

A possible impact of the year-round direct discharge program on the Clark Fork River could be to increase the amount of POC in the river even more due to the direct addition of organic matter in the effluent and due to the gradient of hardness and salinity between the effluent plume downstream of the kraft mill outfall and the ambient river water quality. During the summer of 1984, the Institute of Paper Chemistry noted an increased abundance of caddisflies on both sides of the river immediately downstream of the kraft mill outfall, whereas before the year-round direct discharge program was initiated (April 7, 1984), the increased abundance of caddisflies was only noted on the side of the river influenced by wastewater seepage from the rapid infiltration basins. After deducting the autochthonous inputs of organic matter from the benthos of the Clark Fork River, Ekisola (1985) found that more organic matter accumulated on the river bottom downstream of the kraft mill (in the mixing zone) than upstream of the kraft mill during the autumn of 1984. According to the the water quality data of the Montana Water Quality Bureau (unpublished data, MWQB), there was no sustained pattern of increased concentrations of total volatile solids (another measure of organic matter) downstream of the wastewater mixing zone that could definitely be attributed to the kraft mill except during the spring freshet. The transport of POC might not be a continuous process, but might be a discrete and stochastical (i.e. unpredictable) process. Temporary increases of DOC, POC, and nutrient concentrations had been shown to occur as a result of storm runoff in several streams (Lush and Hynes 1978; Wallace et al. 1982; Casey and Farr 1982; Verhoff et al. 1982). Hence, significant downstream transport of the POC in the Clark Fork River might occur primarily after storm events.

The increased abundance of filter feeders below the kraft mill outfall was similar to abundance patterns observed downstream of lake outlets (Oswood 1976; Sheldon and Oswood 1977; Carlsson et al. 1977; Valett 1985) and fens (Erman and Chouteau 1979). The observed abundance patterns of these filter feeders were believed to be a result of changes in food quality rather than food quantity (Carlsson et al. 1977; Valett 1985). Comparisons of these "natural" gradients of caddisfly abundance to the effects of adding kraft mill wastewater to the river, would imply that the organic matter of the kraft mill wastewater has a high food quality to stream insects. Wotton (1984) suggested that fine POC formed from DOC would have a higher food quality than POC formed from the decomposition of coarser particulate organic carbon. Hence, the kraft mill wastewater could be an important source of food to the stream insects in this reach of the river.

# F. MACROINVERTEBRATE STUDY

# Macroinvertebrate Communities of the Clark Fork River, Montana, 1984-1985

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Final Report

Prepared For

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# INTRODUCTION

This report summarizes information resulting from the analysis of macroinvertebrate samples obtained by staff of the Montana Department of Health and Environmental Sciences (DHES) along the Clark Fork River and tributaries. Most samples were obtained using a modification of Hornig and Pollard's (1978) Standard Traveling Kick Method (STKM) (Appendix I). Deep-water samples were obtained by the use of a petite ponar grab. Five seasons are represented in this study: spring, summer, and fall of 1984 and spring and summer of 1985.

After analysis of the first season's data was underway, a decision was made to replicate all subsequent samples in order to provide information on the reliability (variability) of the data. Four separate samples were obtained and analyzed at each sampling site during each of the remaining four seasons, except in a few instances where breakage during transit or other accident destroyed samples. Montana DHES staff took extensive field notes and photographed each site; they preserved the samples in alcohol and cleaned the samples of plant matter and other debris prior to shipping them to C. E. Hornig for analysis. Beginning with the summer 1984 data, most larger samples were further divided into quarter- or half-replicates and only one quarter or one half per replicate was analyzed.

This was done to save costs and effort, and all data presented in this report have been corrected (multiplied by two for halved replicates and by four for quartered replicates) to reflect this.

Except as indicated above, each individual macroinvertebrate specimen was identified to the lowest practical taxonomic level and the number of individuals present enumerated and recorded.* The taxonomic works consulted are included in the bibliography to this report and a summary list of all species found is included as an appendix. (The raw data have been provided to the Montana DHES over the course of the past two years.) Various statistics were also calculated, with the use of a TRS-80 microcomputer, for purposes of analysis and interpretation. These included percentage distributions for each sample (replicates combined where applicable), Shannon's diversity indices for each sample (Margalef, 1958), and percentage similarity coefficients both among replicates and among sites within a season (Goodall, 1978). These data have also been provided to DHES staff and are summarized in this report.

The data comprise macroinvertebrate community descriptions that can be used to help evaluate impacts of major land and water use patterns occurring within the study area.

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*Many of the Chironomidae identifications should not be considered definitive. However, identifications are consistent throughout the study except as noted in Appendix III.

# OVERVIEW

## Community Structure and Composition

The middle Clark Fork basin supports a rich macroinvertebrate fauna. Over 200 taxa were identified in samples collected in this study, with as many as 60 different taxa present at one time at individual sites. Diversity values ranged well over 4.0, indicating a fairly healthy, not heavily stressed environment at all study sites.

Several factors contribute to the difficulty of interpreting the diversity values, however. First, western Montana is known to support one of the most diverse aquatic insect faunas in North America. The values obtained in the present study may or may not be unusually high for this area. Second, the comparison of diversity values obtained in one study with those obtained in others is very difficult. Taxonomic identifications in particular, especially for midges, may vary greatly in precision and scope. Third, some work has shown that high diversity values may be more indicative of a disturbed than of a pristine ecosystem. The main inference that can be drawn from the diversity values obtained for the Clark Fork River, then, is that the river is not severely degraded. Lesser impacts cannot be ruled out.

Similarity coefficients are a measure of the degree to which two faunal collections are alike in terms of species composition. Both within-site (between-replicate) and among-site similarity coefficients were calculated for this study. The majority of the within-site values were in or near the 70's. Thus, between-site values in the 60's can be considered quite high, approaching those found between replicate collections, whereas those below 40 suggest substantial differences in the fauna. Between-site similarity coefficients (Appendix II) were often high throughout long segments of the Clark Fork, indicating a high degree of faunal consistency.

The presence of large numbers of non-dipteran aquatic insects, such as mayflies, also indicates a stream not heavily stressed by pollutants. However, the high abundance of insects (such as the caddisfly Cheumatopsyche) that are relatively tolerant of pollution and the low diversity (for this part of North America) of the generally pollution-sensitive stoneflies (Plecoptera) suggest a stream that has undergone some degree of pollution impact.

## Productivity

Abundance data at all but the most downstream Clark Fork sites are comparable to data for the Blackfoot River site, ranging from one to several thousand individuals collected per site. Since the invertebrate density of the Blackfoot supports a good trout fishery (Gary Ingman, DHES, personal communication), it is likely that fish food availability is not a limiting factor for Clark Fork salmonid populations.

# DISCUSSION

## Spatial and Seasonal Differences in Macroinvertebrate Populations and Communities

This discussion will center on specific patterns that are apparent between individual taxa and known external environmental factors for a selected group of sites (sites 4 through 9) during one season (summer, 1985) in order to suggest the nature and complexity of such analysis. More general community differences (contrasts in similarity and diversity statistics, shifts in dominant taxa) will be discussed on a broader scale for each season. The general population/environment relationships described, together with information from other systems, can be used as the basis of additional specific interpretations.

### Environment-Population Relationships:
### Sites 4 through 9, Summer 1985

Sites 4 through 9 were chosen for scrutiny because they are tightly spaced along a 9.5-mile reach of river in the vicinity of Missoula, Montana. Additionally, the Missoula Wastewater Treatment Plant (WWTP) represents a major source of nutrient pollution loading to the middle reaches of the Clark Fork River (Gary Ingman, Montana DHES, personal communication.) Summer 1985 was chosen because (1) similarity values were higher among sites 4-9 during summer 1985 than for any other group of sites for any one season; (2) the near-record low water flows of 1985 would tend to maximize the impact of nutrient loading due to increased settling out, lesser dilution, and higher water temperatures; (3) operational problems occurred during this period that resulted in pollution loading exceeding permit limitations (Gary Ingman, DHES, personal communication); (4) thorough site descriptions and substrate photographs were available; and (5) low between-replicate variability for all sites (i.e. high between-replicate similarity coefficients) lent strong credibility to the data. This study was intended both as a means to obtain baseline water-quality information and as a way to assess the impact of specific point sources of pollution, and the conditions listed above provided a good opportunity to illustrate how changes in the macroinvertebrate communities can reflect environmental changes and conditions.

Site 6 had the smallest amount of plant biomass as indicated by site descriptions and photographs of periphyton and laboratory descriptions of organic matter collected. Correspondingly, the total number of invertebrates collected at this site was considerably less than that for the other sites in this group. Because it has the least amount of periphyton of the five sites, site 6 can be considered a good reference site for looking at the response of individual invertebrate populations to increases in primary productivity and, more importantly, because of the radically different quality of the periphyton between sites 4, 5 and 6 (upstream of the Missoula WWTP) on the one hand and sites 8 and 9 (downstream of the WWTP) on the other, site 6 is also a good reference for assessing population response to the type or quality of organic material present (i.e. location relative to the WWTP). Additionally, site 6 is the furthest downstream site--and thus the most distant from known sources of heavy metal pollution located upstream--of those sites upstream from the Missoula WWTP. Finally, site 6 also has the highest average similarity to each of the other sites for summer 1985 (47%). For these reasons site 6 was chosen as the reference site for purposes of this discussion and site 6 data will be presented first.

### Macroinvertebrates and Substrate of Site 6

The site 6 macroinvertebrate collection for summer 1985 is rich in taxa (61 total) with a relatively high diversity (4.0). The community structure generally fits the pattern of an unstressed or lightly stressed community, i.e. there are a few abundant taxa but no single taxon is overwhelmingly dominant. Excluding the 10 most common taxa, no single taxon contributes more than one percent of the collection.

There are three co-dominants (Cheumatopsyche, Symphitopsyche cockerelli, and Baetis insignificans) in this collection, constituting in total 55% of the individuals collected. This confirms the representativeness of site 6 in that one or the other of these three taxa is the most abundant taxon at each of the Clark Fork sites between 4 and 25. The four taxa next most abundant at site 6 (Baetis tricaudatus, Polypedilum, Hydropsyche occidentalis, and Tricorythodes minutus) were also commonly found at many sites down to site 21.

The substrate at site 6 consisted of many large cobbles (over 256 mm) and a considerable amount of fines interspersed among the cobbles. The cobbles were well cemented to the underlying material. Periphyton, although present, was not luxuriant and only covered 60% of rocks. It was difficult to scrape off, with half the material consisting of diatoms. Replicate one had somewhat more organics and a correspondingly higher count of total numbers and of hydropsychid caddisflies. Otherwise there was little difference between the replicates in faunal composition, as reflected in high between-replicate similarity coefficients, or in quantity of material or insects collected.

## Macroinvertebrates and Substrate, Sites 4, 5, 8 and 9

Site 4 - The substrate at this site, located just downstream of Milltown Dam, was luxuriant with periphytic growth. This growth was qualitatively very different from the growth smothering the substrate at site 8 and resembled that found at site 6. The substrate was somewhat cemented. Absolute counts of macroinvertebrates were more than double those obtained for site 6.

Site 5 - The amount of periphyton at this site was intermediate between that at site 4 and at site 6 but similar in type to that found at these two sites. The total number of organisms collected was also intermediate between that for site 4 and that for site 6.

Site 8 - Although the rocks were well embedded, this site was characterized by very heavy periphyton growth that can be considered a potential cause for the doubling in total abundance at this site in comparison to site 6.

Site 9 - Periphyton and total abundance were both intermediate between that found at site 6 and that found at site 8.

## Variations in Community Composition, Sites 4-9

The communities at these five sites are generally similar, as expressed in high between-site similarity coefficients. The proportion of the collection made up of the dominant hydropsychid (net-spinning caddisfly) taxa remained relatively constant. Several other common taxa, however, appeared to respond differently to changes in substrate or periphyton characteristics, including rock size and quality or type (as well as quantity) of organic matter.

Taxa which may be considered candidates for indicating changes in conditions created by nutrient loading from the Missoula WWTP are those which have populations that respond differentially to the periphytic accumulations at site 8 versus site 4: *Optioservus*, *Zaitzevia*, *Micropsectra*, *Chironomus*, *Cricotopus*, and *Serratella tibialis*. *S. tibialis* is a particularly prime candidate because of its opposite responses to the two types of periphyton (i.e. it seems to respond positively to the type of periphyton found upstream of the WWTP and negatively to that found downstream). Changes in the community composition involving such species should be watched closely for evidence that nutrient loading is increasing.

## General Spatial Patterns, Summer 1985 Collections

The greatest differences in biota relative to the remainder of the river were found at the most downstream sites, 27 and 31. The dominant taxa at site 27 reflected the effects of dam release on invertebrate collections: Cladocerans, probably "refugees" from the reservoir, were the dominant taxon, with other abundant taxa consisting of midges, beetles, and worms. Site 31 biota reflected the depositional nature of this site. The most abundant taxon here was *Paraleptophlebia bicornuta*, a leptophlebiid mayfly equipped with tusks for adaptation to a burrowing habit. The next two must abundant taxa were a Chrionominae midge and the mayfly *Tricorythodes minutus*, whose gills are adapted to avoid damage or smothering from sand or silt.

A very substantial change in faunal composition also occurred downstream of the Flathead River (sites 24 and 25), where *Cheumatopsyche* was the only upstream-abundant taxon that remained dominant. Dramatic abundance decreases occurred for *Symphitopsyche cockerelli* and *Baetis insignificans*, two highly abundant taxa at all Clark Fork sites upstream of the Flathead. Snails were common elements at sites 24 and 25, while they were not found upstream of these sites. In general, the fauna of the Clark Fork below the vicinity of site 21 shifted from one dominated by mayflies and caddisflies to one dominated by midges or snails. Diversity, however, did remain high, with 55 taxa collected at site 24 and 35 taxa at site 31.

The dominance patterns from the middle reaches of this survey (sites 11-15 in the vicinity of Frenchtown) were somewhat distinct from both upstream sites (4-9) and downstream sites (19-25) in that *Cheumatospsyche*, although still common, dropped in abundance and was no longer the first or second most abundant taxon (Fig. 1). *Baetis insignificans*, consistently abundant from sites 1 to 21, occupied the position of most-dominant taxon at sites 11-15. The fast colonization rates known to be characteristic of *Baetis* mayflies may partly explain their consistently high populations. The fairly common mayfly *Nixe simplicioides* showed a trend opposite to that exhibited by *Cheumatopsyche*, dramatically increasing in abundance at these sites (Fig. 2).

Faunal composition of summer collections from the mouths of the major Clark Fork tributaries are quite distinct. The Blackfoot River site (site 2) was highly dominated by a Tanytarsini midge. Chief components of the Bitterroot River (site 10) collection were blackflies, riffle beetles, and *Baetis* mayflies. Samples from the slow-moving Flathead River (site 23) were predominately snails (a different genus than that common in the Clark Fork), amphipods, aquatic earthworms, and the mayflies

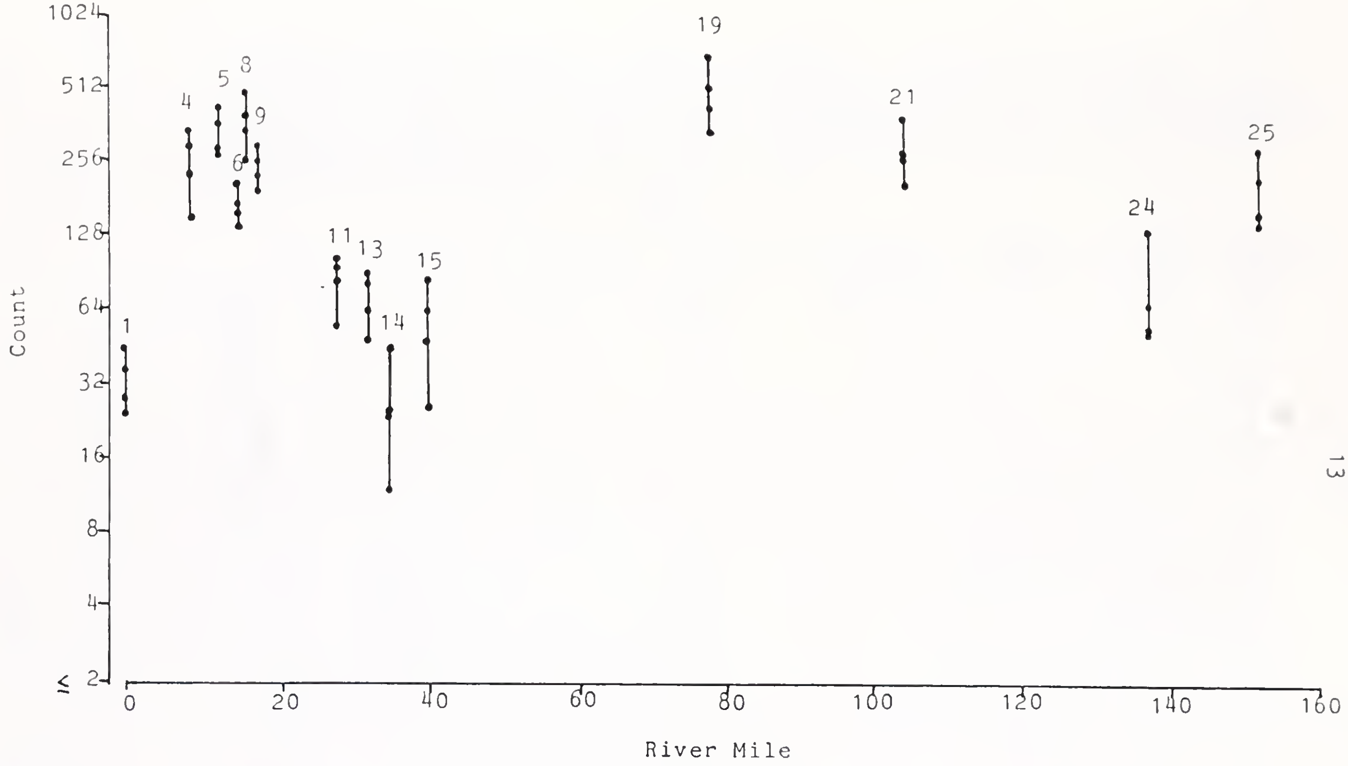

Figure 1. Cheumatopsyche counts at middle reach, Clark Fork River study sites, summer 1985. (Excludes tributary and far downstream sites.) Four replicate samples were taken at each site; dots represent individual replicate counts and vertical lines represent ranges of counts obtained at each site. Numbers above data points represent site numbers (Appendix IV).

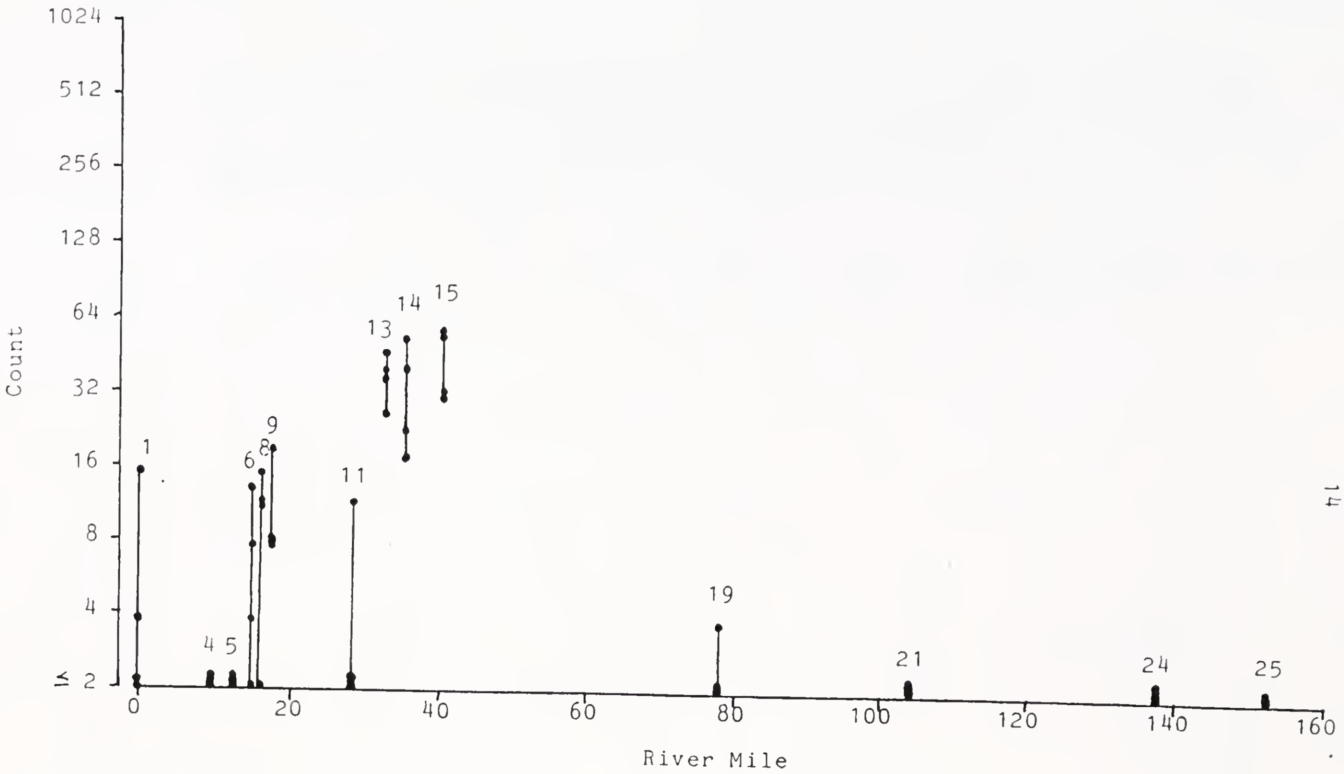

Figure 2. *Nixe simplicioides* counts at middle reach, Clark Fork River study sites, summer 1985. (Excludes tributary and far downstream sites.) Four replicate samples were taken at each site; dots represent individual replicate counts and vertical lines represent ranges of counts obtained at each site. Numbers above data points are site numbers.

*Stenonema* and *Paraleptophlebia bicornuta* also found in the lower Clark Fork. Because these tributaries (with the exception of the Flathead) support abundant and diverse invertebrate populations that include individuals of most species found in the mainstem, they can be considered an important source of potential recolonization populations in the event of catastrophe striking the Clark Fork.

### Comparison with Summer 1984 Survey Fauna

The large differences in the hydrograph between summer 1984 and summer 1985 were reflected in major changes in the invertebrate composition of the Clark Fork River between these two years. The fauna generally shifted away from collector-gatherer mayflies to collector-filterer net-spinning caddisflies (Hydropsychidae) during summer 1985. Figures 3 and 4, in comparison to Figures 1 and 2 presented earlier, demonstrate this shift for the caddisfly *Cheumatopsyche* and the common mayfly *Nixe simplicioides*. This shift might be explained in terms of substrate, flow, and food conditions favoring large populations of the resident hydropsychids, in turn preventing the establishment of the mayflies in large numbers.

Although the Clark Fork summer residents underwent large alterations in abundance between 1984 and 1985, the

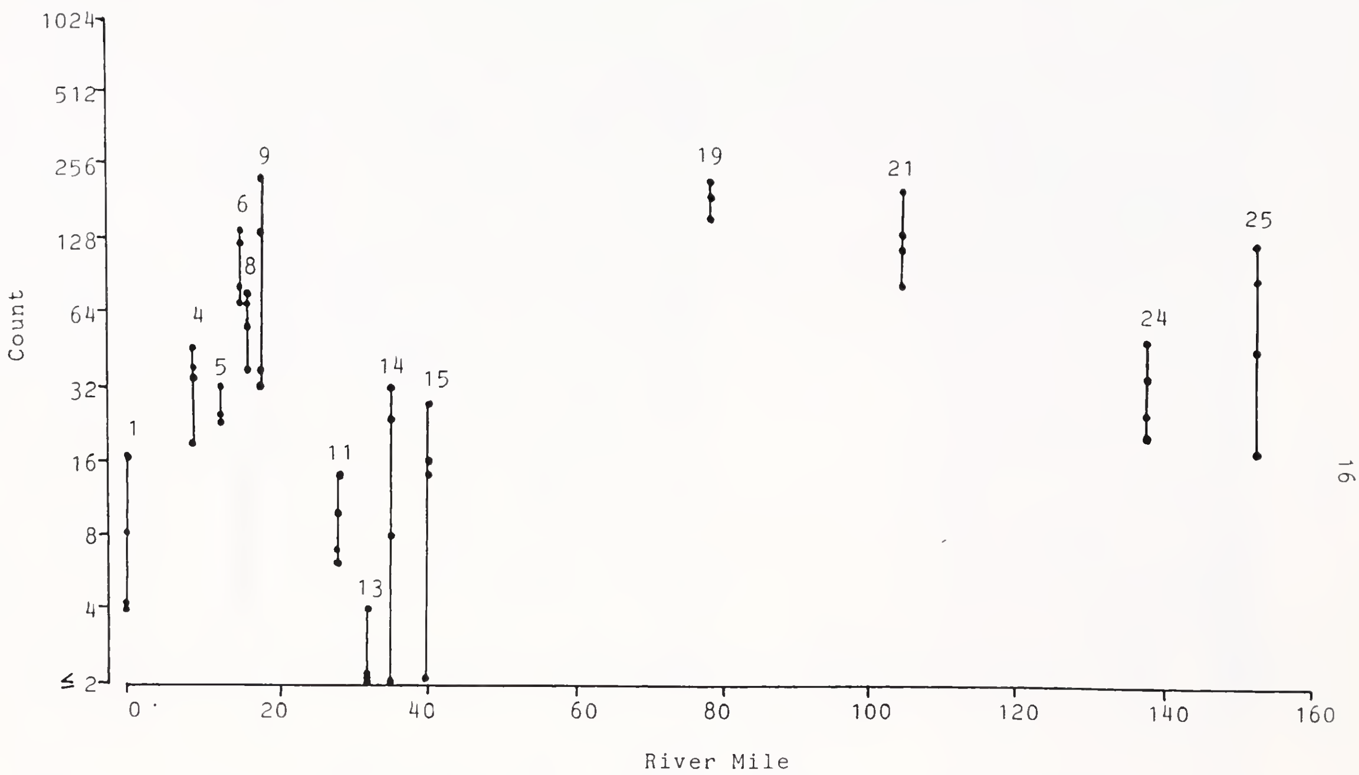

Figure 3 . *Cheumatopsyche* counts at middle reach, Clark Fork River study sites, summer 1984. (Excludes tributary and far downstream sites.) Four replicate samples were taken at each site except sites 5 and 19, for which only three replicates are available; dots represent individual replicate counts and vertical lines represent ranges of counts obtained at each site. Numbers above data points are site numbers.

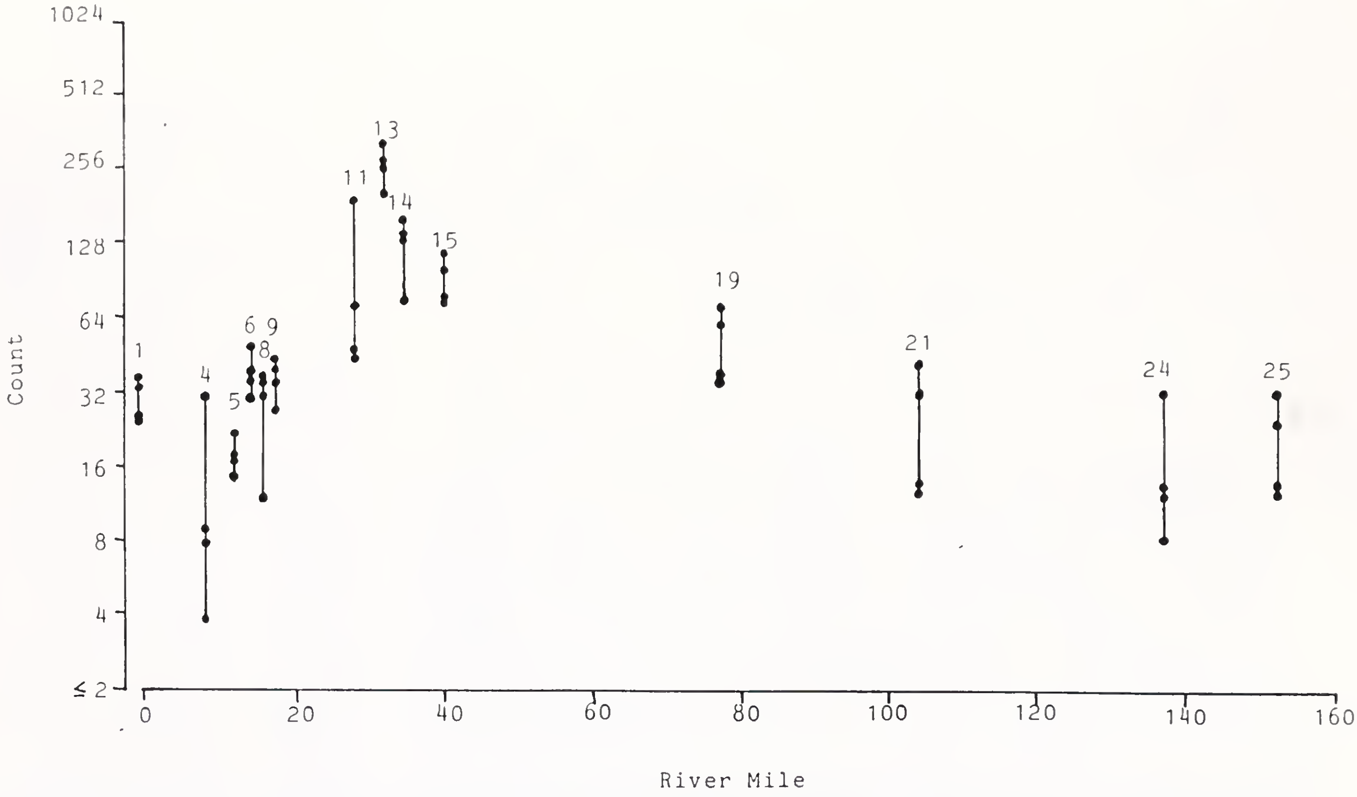

Figure 4 . *Nixe simplicioides* counts at middle reach, Clark Fork River study sites, summer 1984. (Excludes tributary and far downstream sites.) Four replicate samples were taken at each site; dots represent individual replicate counts and vertical lines represent ranges of counts obtained at each site. Numbers above data points are site numbers.

common taxa were all present in both years. More importantly, as comparison of Figures 1 and 2 with 3 and 4 will again illustrate, the general spatial differences trends--i.e. the general pattern of longitudinal variation in fauna upstream or downstream along the Clark Fork--remained constant. The richness of taxa and degree of dominance, as reflected in the diversity values, were also very similar in summer 1984 and summer 1985, especially for sites 1 to 11 (Figure 5).

Because the Nixe simplicioides population is particularly high at site 13 and to a lesser extent at sites 14 and 15, this species may have been responding to the impact of Champion Mill effluent and it is recommended that this be kept in mind in future years. However, this may also be simply a response to naturally occurring conditions reaching optimum at about the location of site 13. Note that N. simplicioides numbers began to increase upstream of the mill at site 11.

## Comparisons with Other Seasons: Spring 1984, Spring 1985, Fall 1984 Data

The seasonal succession of Clark Fork insects follows the typical pattern of a fast-life-cycle summer fauna and a slow-life-cycle fall-through-spring fauna characteristic of most temperate streams. During the fall through spring

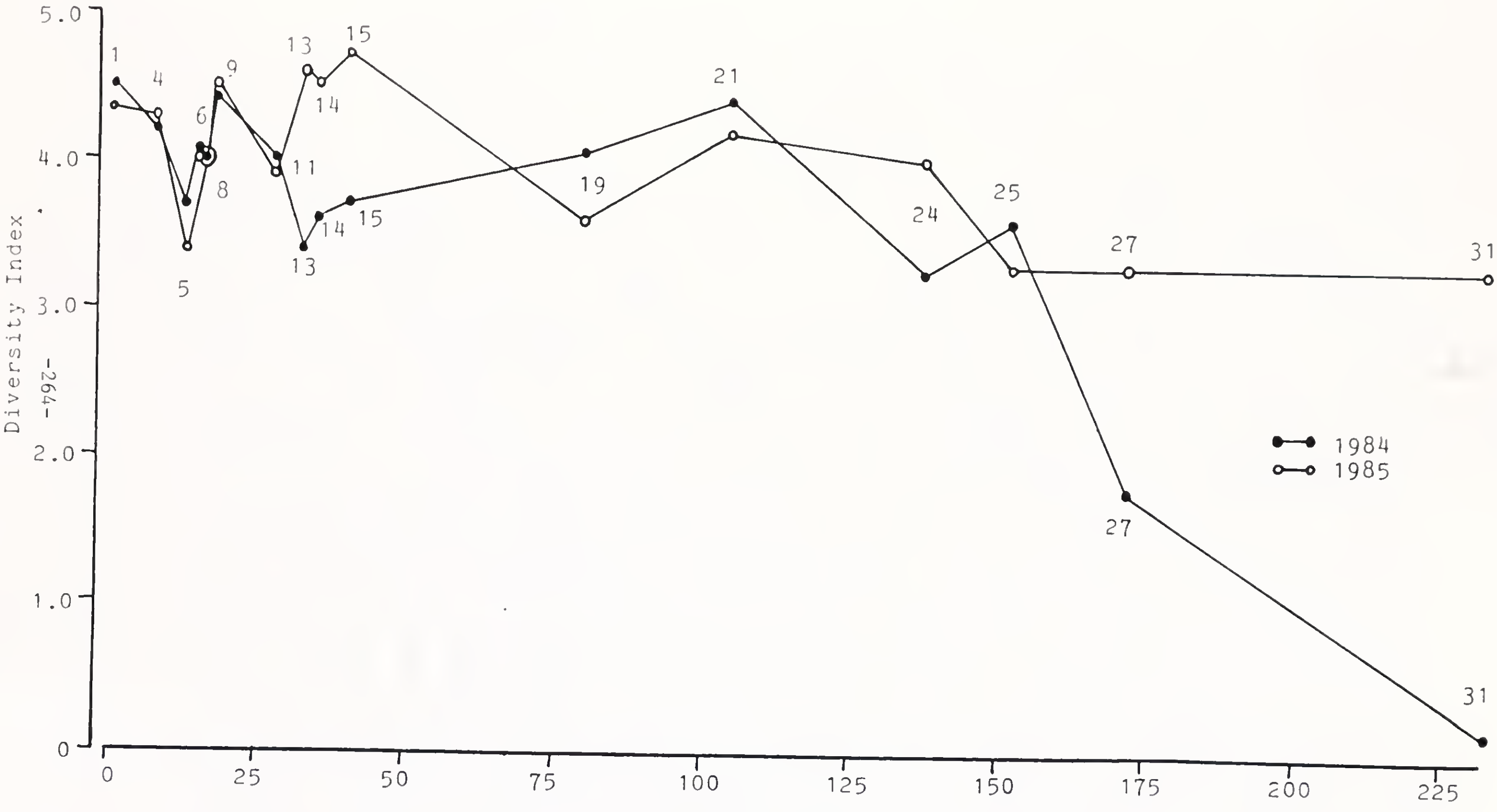

Figure 5 . .Species diversity index values for summer 1984 and 1985 samples, Clark Fork River, Montana. (Data for replicate samples have been combined.) The location of the farthest downstream site shown was changed to a more favorable area between 1984 and 1985. Numbers near data points are site numbers.

months, the river water is relatively homogeneous throughout most of its length, particularly in terms of current and temperature. As a result, longitudinal gradation of the fauna is relatively less than that found in the summer. During the summer, a distinct gradient of temperature occurs and flows are low enough to create a large variety of habitats (shallow riffles, pools, runs, and all gradients in between). During the higher flow conditions of spring, the river becomes one long fast-flowing run with little development of pools or shallow riffles. The more consistent conditions in the spring or fall result in a greater dominance of the more adaptable taxa, lowering diversity indices throughout the system compared to the summer (Figures 6, 7). Between-site similarities also tend to be higher in the fall due to the greater uniformity of water quality and substrate conditions (see Appendix II).

_Ephemerella infrequens_ dominated the majority of sites between 1 and 21 during spring 1984, fall 1984, and spring 1985. In general, hydropsychid caddisflies are relatively much less important during fall and spring, while mayflies become correspondingly more important.

Spring 1985--As with summer 1985 collections, the dominant taxa from sites 19 and 21 are more similar to those upstream of site 11 than to those in the vicinity of

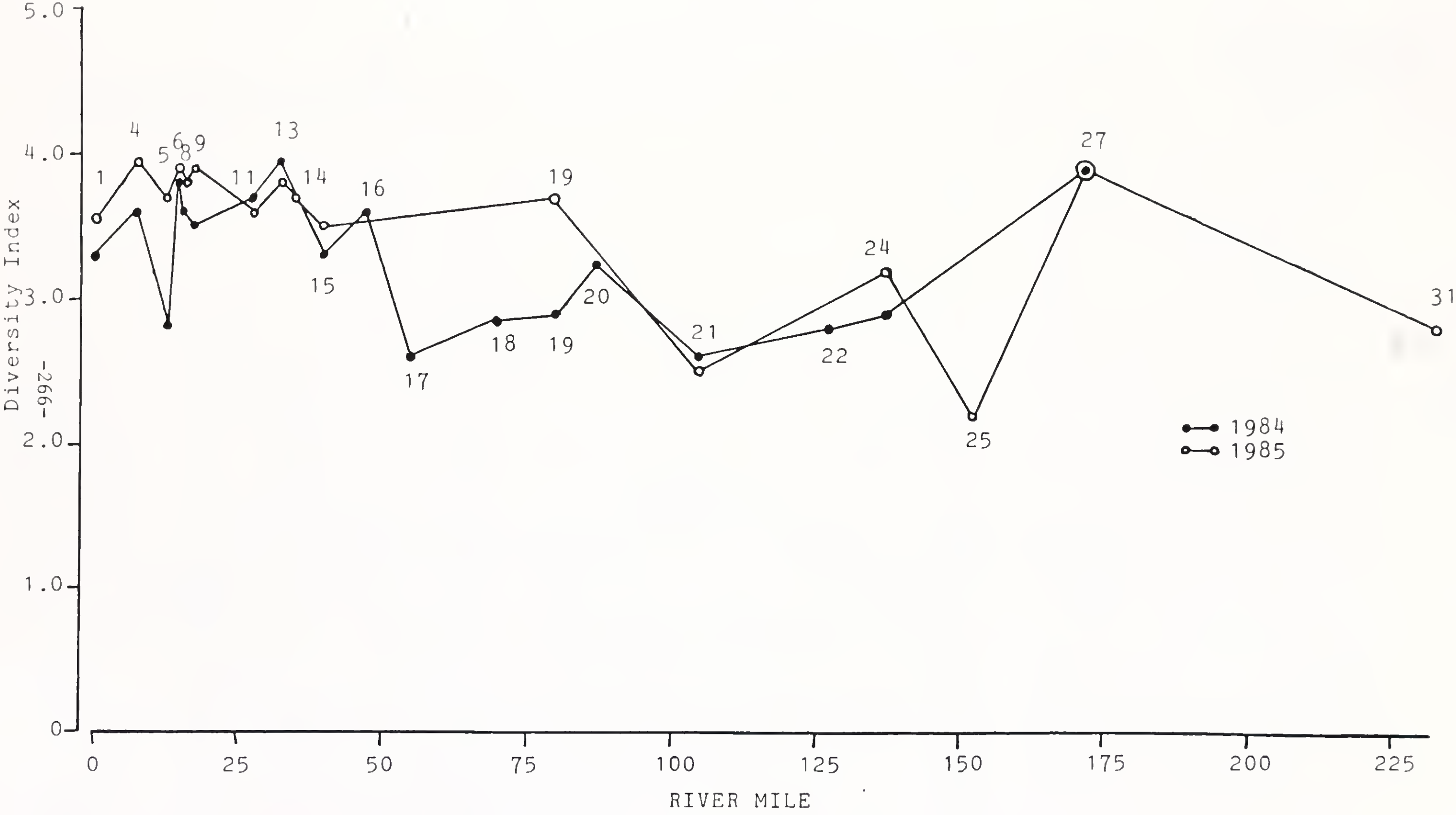

Figure 6. Species diversity index values for spring 1984 and 1985 samples, Clark Fork River, Montana. (Data for replicate samples taken in 1985 have been combined.) Numbers near data points are site numbers.

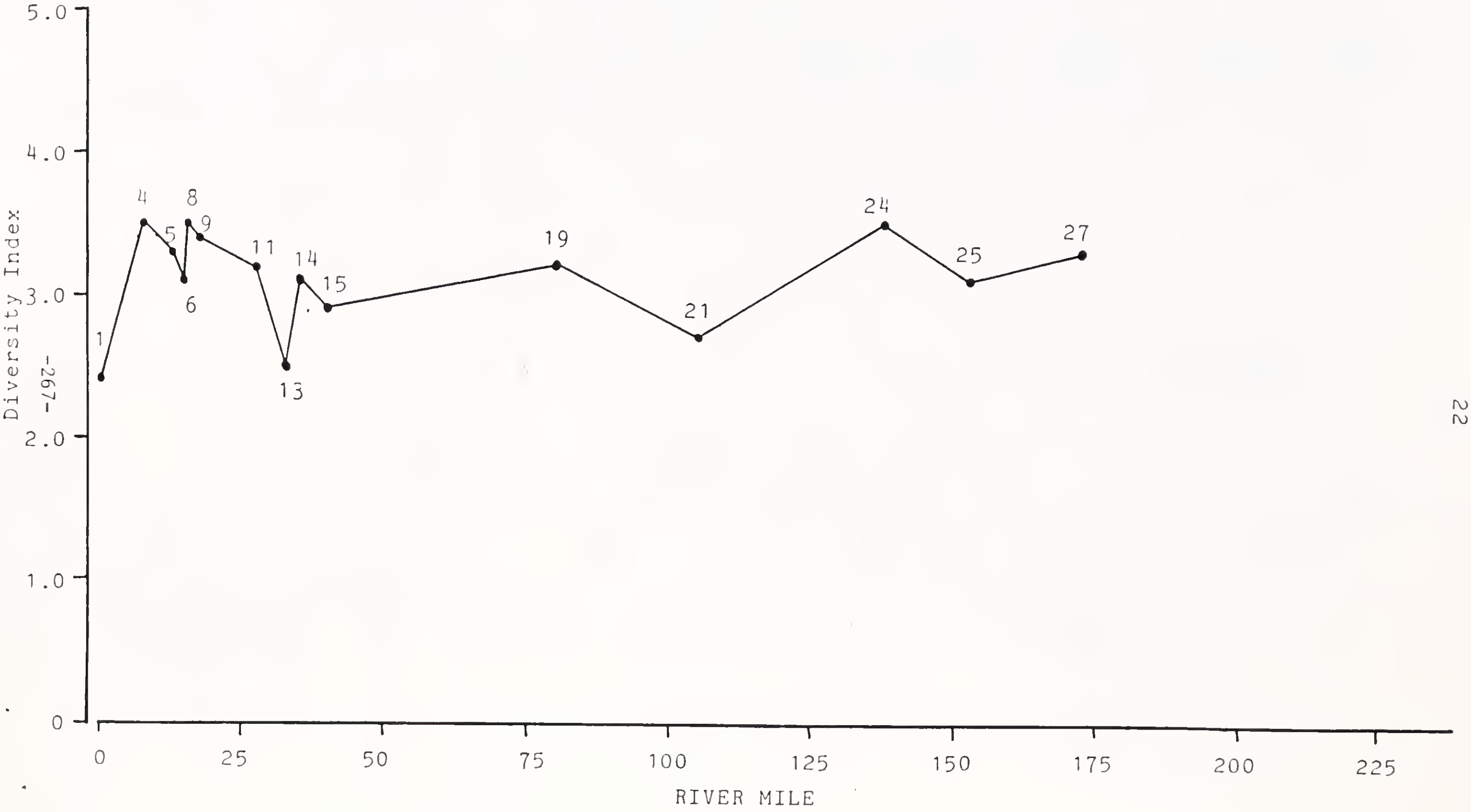

Figure 7. Species diversity index values for fall 1984 samples, Clark Fork River, Montana. (Data for replicate samples have been combined.) Numbers near data points are site numbers.

Frenchtown (sites 11-15). At these sites, the midge Orthocladius obumbratus greatly increases in abundance, replacing even Ephemerella infrequens as the most abundant taxon. O. obumbratus also dominates the collections taken below Flathead River. The pollution-sensitive winter stonefly (Capniidae) is common at most sites upstream of the Flathead, suggesting that pollution is not significant at this time.

Spring 1984--The lower numbers collected during spring 1984 compared to the other seasons is an artifact of sampling effort. During this intial survey, only one sample, rather than four, was taken at each site, and although each spring 1984 sample covered a larger substrate area than subsequent samples, the results still cannot be considered comparable in terms of sampling effort. However, community composition data (relative abundances) can be compared with that of other seasons since the basic sampling method was identical.

Diversity indices remained quite similar at comparable sites. (Sites 6, 15, 21, and 31 were subsequently moved.) The overall dominance pattern in the Frenchtown area (sites 11-15), however, was not the same as for 1985. The sites were not dominated by O. obumbratus but instead followed the same pattern of Emphemerella infrequens/Baetis tricaudatus dominance characteristic of all the sites from

1 to 21. Among the stoneflies, the perlodid Isoperla fulva was relatively more abundant and Capnia relatively less abundant in spring 1984 in comparison to spring 1985.

Fall 1984--The fall 1984 collections contained much higher numbers of invertebrates than other seasons. Fall is a "recruitment" season for the fall-to-spring fauna, with spring fauna consisting of the survivors of those hatched in fall. Between-site similarity coefficients were very high, approaching the within-site similarities (Appendix II), attributable largely to the preponderance of the mayflies Ephemerella infrequens and Baetis tricaudatus. As these same mayflies dominate the Blackfoot and Bitterroot collections (sites 2 and 10), there was especially high similarity between these and the Clark Fork collections during this season.

As for other seasons, the fauna below the Flathead and again below Thompson Falls Dam was quite distinct from that of the upstream Clark Fork River (sites 1 to 21). For example, the mayfly Stenenema (a genus more typical of the eastern U.S.) reached very high numbers at site 25 but was almost nonexistent upstream of the Flathead.

Diversity values show a sharp drop at site 13 compared to neighboring sites, and similarities were typically very low (average 35) for this site. The algal-feeding caddisfly Hydroptila and the large-cased midge

Microtendipes reached their highest numbers at this site and Ephemerella infrequens its lowest number. For Hydroptila, this may have been a naturally occurring optimum; however, the Microtendipes pattern does not fit this hypothesis and the E. infrequens follows a classic impact-recovery pattern with a sudden drop in numbers at site 13 and gradual increase through sites 14 and 15. Oligochaeta, Hydropsyche, Symphitopsyche, Isogenoides, and Rhithrogena populations also seem to have responded to changed environmental conditions between sites 11 and 13. The possibility of impact from Champion Mill effluent during this season should be considered. Although at this time the impact can be classified as subtle and does not approach those often found downstream of major pollutant outfalls, the taxa noted above as seeming to be responsive to changed conditions should be monitored with especial care, like the sensitive taxa identified above from summer 1984 data for sites 4-9. These alterations in similarity and diversity occurring downstream from Champion Mill are evident only in the fall 1984 data.

## Ponar Samples

### Pools

During summer 1984 (only), ponar samples were taken at several Clark Fork River pools in order to assist in the evaluation of the possible effects of Champion Mill on Clark Fork water quality. Sample sizes were small (10-150 individuals in each sample) and the area of bottom habitat sampled was limited, precluding the inference of definitive conclusions. Patterns of faunal richness and abundance appeared to be most closely related to the type of substrate material collected with the specimens, however, rather than to proximity to the mill. Those samples containing finer materials tended to have higher numbers of individuals and more different species than those samples containing mostly gravel. Most abundant taxa collected were Oligochaetes (especially evident in samples containing organics) and the Chironomids *Phaenopsectra* and *Microtendipes*. (*Phaenopsectra* was most abundant at sites closest to Champion Mill and further study of its indicator potential might be warranted.) The mayfly *Nixe simplicioides* was frequently found among these Clark River pool sites. These data do not provide evidence of any water quality impact attributable to Champion Mill.

## Reservoir Ponar Samples

Ponar samples were also taken throughout the study from reservoirs along the Clark Fork River. As would normally be expected in reservoirs, midges and aquatic worms made up virtually all of the organisms collected. Samples from Thompson Falls and Cabinet Gorge reservoirs yielded a rich midge fauna plus a few scattered insects of other types (total number of taxa collected over five seasons was 35 for Thompson Falls and 34 for Noxon Rapids). In contrast, Milltown and Noxon Rapids yielded very sparse collections (only 16 and 14 taxa, respectively).

Oligochaetes were the most frequently and abundantly collected, with numbers reaching well into the hundreds at a given site and season. Of the midges, the predaceous _Procladius_ was frequently and often abundantly collected at all but Milltown Reservoir, where it was not seen, and _Chironomus_ was frequently and often abundantly collected at all but Cabinet Gorge Reservoir, where it was not found. A few other midges were abundant on a more local and/or a more seasonal basis (for example _Polypedilum_ and _Paralauterborniella_ during summer collections at Thompson Falls).

Milltown Reservoir collections never contained much other than Oligochaetes and _Chironomus_ midges; Noxon Reservoir collections never contained much other than Oligochaetes and _Chironomus_ and _Procladius_ midges. Cabinet Gorge Reservoir collections generally contained diverse fauna (except during spring of 1985, when only two specimens of one midge taxon were collected). Thompson Falls Reservoir yielded diverse collections at all times.

These collections indicate a severely stressed environment at Milltown Reservoir, a somewhat stressed but improved environment at Noxon Reservoir (where Procladius was present), and generally favorable environments at Thompson Falls and Cabinet Gorge Reservoirs (with the exception of the anomalous collection from Cabinet Gorge for spring 1985).

A master list of all species collected by both kick and ponar techniques, with indications as to which species are dominant by stream reach, is incorporated as Appendix III of this report. Appendix IV presents information on the sampling stations in the form of a table.

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# Appendix I. Description of the Modified Traveling-Kicknet Macroinvertebrate Sampling Technique Used in the Lower Clark Fork Study*

The technique used in this study for collection of benthic macroinvertebrate samples was a modification of a method described by Kinney et al (1977)[1]. An aquatic "D"-net (Ward's 10W0620) with a 36 centimeter (cm) long nylon net composed of 9 strands/cm (22 mesh) was used to collect untimed, approximately equal-surface area kick samples of Clark Fork mainstem and major tributary macrobenthos.

Samples were collected by holding the net at arms length in front of and downstream from the investigator while traveling slowly downstream and vigorously kicking and overturning the streambed material to a depth of several inches. The entire contents of the net were transferred to pint or quart glass jars, preserved in 70% ethanol and returned to the laboratory for sorting, organism counting and species identifications.

Five samplings were conducted at each of the shallow-water biological monitoring stations on a seasonal basis from March 1984 to August 1985. During the initial sampling (Spring 1984), only one sample was collected from each station. Approximately 4 square feet was disturbed in an area of moderately fast current (about 1.5 to 2.5 ft./sec.) followed by the disturbing of about two square feet in slow to moderate current (about 0.5-1.5 ft./sec.). The combined sampling constituted one sample; the net contents were transferred to the sample jar after each area had been sampled. Where possible, rich sites (those with piles of rocks providing a large area for colonization) were selected at each station. Riffles were selected for the moderately fast water samplings whenever available.

During subsequent seasonal samplings (summer, fall 1984; spring, summer 1985), four smaller surface area replicates were collected at each station in order to increase the statistical reliability of the data. Each replicate was collected by disturbing about two square feet in moderately fast current followed by about one square foot in slow to moderate current. Organisms were identified and counted in each replicate. However, for purposes of data analysis, results of the four replicates were pooled.

## References

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*This description was provided by staff of the Montana Department of Health and Environmental Sciences.

# APPENDIX II

# SIMILARITY COEFFICIENTS

| Site Number | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 13 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 24 | 27 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | | | | |
| 2 | 55 | | | | | | | | | | | | | | | | | | | |
| 4 | 59 | 55 | | | | | | | | | | | | | | | | | | |
| 5 | 57 | 54 | 68 | | | | | | | | | | | | | | | | | |
| 6 | 61 | 59 | 70 | 54 | | | | | | | | | | | | | | | | |
| 8 | 66 | 43 | 55 | 40 | 66 | | | | | | | | | | | | | | | |
| 9 | 64 | 40 | 54 | 38 | 65 | 83 | | | | | | | | | | | | | | |
| 10 | 50 | 43 | 45 | 33 | 57 | 53 | 53 | | | | | | | | | | | | | |
| 11 | 70 | 50 | 49 | 44 | 62 | 71 | 68 | 56 | | | | | | | | | | | | |
| 13 | 66 | 49 | 55 | 51 | 56 | 64 | 59 | 59 | 72 | | | | | | | | | | | |
| 15 | 67 | 37 | 42 | 44 | 49 | 68 | 69 | 46 | 69 | 73 | | | | | | | | | | |
| 16 | 54 | 31 | 36 | 27 | 50 | 67 | 68 | 60 | 68 | 56 | 64 | | | | | | | | | |
| 17 | 59 | 35 | 42 | 34 | 52 | 67 | 69 | 51 | 67 | 53 | 68 | 72 | | | | | | | | |
| 18 | 70 | 43 | 57 | 47 | 58 | 62 | 62 | 52 | 66 | 57 | 63 | 52 | 72 | | | | | | | |
| 19 | 62 | 33 | 42 | 36 | 53 | 68 | 67 | 42 | 65 | 51 | 65 | 63 | 80 | 71 | | | | | | |
| 20 | 68 | 40 | 51 | 53 | 59 | 62 | 60 | 42 | 69 | 56 | 64 | 60 | 60 | 72 | 71 | | | | | |
| 21 | 66 | 36 | 40 | 43 | 49 | 56 | 59 | 39 | 60 | 49 | 66 | 61 | 73 | 74 | 81 | 77 | | | | |
| 22 | 51 | 22 | 24 | 28 | 35 | 54 | 58 | 37 | 52 | 54 | 69 | 57 | 63 | 58 | 68 | 62 | 74 | | | |
| 24 | 7 | 7 | 7 | 6 | 10 | 10 | 12 | 10 | 14 | 9 | 8 | 16 | 9 | 9 | 16 | 17 | 20 | 22 | | |
| 27 | 4 | 22 | 14 | 6 | 27 | 19 | 21 | 24 | 15 | 11 | 13 | 23 | 18 | 10 | 12 | 12 | 9 | 9 | 18 | |

Figure IA. Similarity coefficients for kick samples taken during spring of 1984, Clark Fork River and tributaries (x 100). Coefficients greater than 40 are underlined; those greater than 60 are double-underlined.

| Site Number | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 13 | 14 | 15 | 19 | 21 | 23 | 24 | 25 | 27 | 31 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | | | |
| 2 | 40 | | | | | | | | | | | | | | | | | | |
| 4 | 60 | 53 | | | | | | | | | | | | | | | | | |
| 5 | 43 | 33 | 63 | | | | | | | | | | | | | | | | |
| 6 | 44 | 27 | 53 | 55 | | | | | | | | | | | | | | | |
| 8 | 35 | 26 | 40 | 41 | 57 | | | | | | | | | | | | | | |
| 9 | 53 | 36 | 54 | 54 | 67 | 56 | | | | | | | | | | | | | |
| 10 | 51 | 47 | 49 | 42 | 46 | 32 | 50 | | | | | | | | | | | | |
| 11 | 51 | 35 | 46 | 36 | 41 | 30 | 57 | 64 | | | | | | | | | | | |
| 13 | 39 | 17 | 27 | 27 | 48 | 33 | 42 | 44 | 43 | | | | | | | | | | |
| 14 | 39 | 27 | 31 | 30 | 43 | 35 | 58 | 47 | 58 | 54 | | | | | | | | | |
| 15 | 48 | 31 | 39 | 33 | 41 | 34 | 58 | 53 | 77 | 48 | 66 | | | | | | | | |
| 19 | 40 | 24 | 37 | 40 | 66 | 41 | 61 | 40 | 46 | 44 | 49 | 45 | | | | | | | |
| 21 | 41 | 26 | 38 | 45 | 63 | 42 | 63 | 40 | 34 | 40 | 50 | 35 | 69 | | | | | | |
| 23 | 8 | 6 | 7 | 10 | 15 | 12 | 12 | 13 | 12 | 15 | 27 | 14 | 21 | 25 | | | | | |
| 24 | 20 | 14 | 23 | 28 | 50 | 32 | 42 | 27 | 25 | 25 | 41 | 29 | 50 | 56 | 34 | | | | |
| 25 | 25 | 14 | 19 | 27 | 58 | 34 | 41 | 38 | 27 | 36 | 37 | 32 | 52 | 57 | 24 | 52 | | | |
| 27 | 7 | 5 | 5 | 6 | 10 | 10 | 8 | 8 | 6 | 14 | 9 | 7 | 13 | 10 | 12 | 9 | 12 | | |
| 31 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 2 | 69 | |

Figure IB. Similarity coefficients for kick samples taken during summer of 1984, Clark Fork River and tributaries (x 100). Coefficients greater than 40 are underlined; those greater than 60 are double-underlined. (Replicate data for each site combined.)

| Site Number | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 13 | 14 | 15 | 19 | 21 | 23 | 24 | 25 | 27 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | | |
| 2 | 49 | | | | | | | | | | | | | | | | | |
| 4 | 53 | 46 | | | | | | | | | | | | | | | | |
| 5 | 68 | 57 | 75 | | | | | | | | | | | | | | | |
| 6 | 65 | 54 | 59 | 65 | | | | | | | | | | | | | | |
| 8 | 59 | 52 | 61 | 70 | 65 | | | | | | | | | | | | | |
| 9 | 59 | 55 | 63 | 68 | 80 | 74 | | | | | | | | | | | | |
| 10 | 45 | 44 | 70 | 60 | 53 | 53 | 60 | | | | | | | | | | | |
| 11 | 62 | 52 | 57 | 67 | 58 | 69 | 71 | 61 | | | | | | | | | | |
| 13 | 16 | 23 | 26 | 21 | 24 | 32 | 33 | 33 | 49 | | | | | | | | | |
| 14 | 37 | 38 | 55 | 48 | 51 | 55 | 61 | 59 | 70 | 64 | | | | | | | | |
| 15 | 68 | 52 | 58 | 69 | 64 | 74 | 73 | 60 | 87 | 44 | 67 | | | | | | | |
| 19 | 57 | 54 | 60 | 65 | 73 | 73 | 81 | 63 | 76 | 39 | 69 | 80 | | | | | | |
| 21 | 66 | 50 | 49 | 57 | 74 | 67 | 70 | 52 | 66 | 37 | 58 | 72 | 76 | | | | | |
| 23 | 3 | 10 | 5 | 6 | 6 | 11 | 10 | 8 | 12 | 10 | 12 | 8 | 7 | 5 | | | | |
| 24 | 7 | 18 | 16 | 16 | 19 | 23 | 22 | 18 | 21 | 18 | 22 | 19 | 20 | 20 | 21 | | | |
| 25 | 5 | 17 | 27 | 15 | 27 | 25 | 35 | 30 | 24 | 26 | 36 | 24 | 31 | 29 | 16 | 40 | | |
| 27 | 5 | 17 | 28 | 19 | 31 | 28 | 32 | 27 | 19 | 20 | 30 | 19 | 30 | 25 | 11 | 30 | 51 | |

Figure IC. Similarity coefficients for kick samples taken during fall of 1984, Clark Fork River and tributaries (x 100). Coefficients greater than 40 are underlined; those greater than 60 are double-underlined. (Replicate data for each site combined.)

| Site Number | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 13 | 14 | 15 | 19 | 21 | 23 | 24 | 25 | 27 | 31 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | | | |
| 2 | 39 | | | | | | | | | | | | | | | | | | |
| 4 | 42 | 30 | | | | | | | | | | | | | | | | | |
| 5 | 55 | 40 | 58 | | | | | | | | | | | | | | | | |
| 6 | 65 | 33 | 43 | 46 | | | | | | | | | | | | | | | |
| 8 | 66 | 43 | 34 | 44 | 63 | | | | | | | | | | | | | | |
| 9 | 56 | 44 | 53 | 62 | 57 | 57 | | | | | | | | | | | | | |
| 10 | 52 | 41 | 36 | 51 | 55 | 52 | 43 | | | | | | | | | | | | |
| 11 | 56 | 37 | 48 | 64 | 46 | 48 | 56 | 48 | | | | | | | | | | | |
| 13 | 57 | 36 | 39 | 45 | 64 | 58 | 56 | 51 | 64 | | | | | | | | | | |
| 14 | 47 | 33 | 42 | 48 | 53 | 43 | 57 | 40 | 63 | 79 | | | | | | | | | |
| 15 | 44 | 40 | 39 | 46 | 49 | 40 | 58 | 38 | 59 | 75 | 84 | | | | | | | | |
| 19 | 62 | 53 | 51 | 61 | 52 | 56 | 68 | 44 | 60 | 56 | 51 | 53 | | | | | | | |
| 21 | 52 | 24 | 30 | 33 | 58 | 50 | 39 | 49 | 31 | 47 | 36 | 34 | 42 | | | | | | |
| 23 | 18 | 15 | 18 | 17 | 17 | 16 | 17 | 14 | 32 | 32 | 31 | 31 | 17 | 13 | | | | | |
| 24 | 27 | 36 | 29 | 21 | 26 | 41 | 36 | 22 | 45 | 52 | 52 | 55 | 39 | 19 | 35 | | | | |
| 25 | 20 | 20 | 18 | 13 | 20 | 31 | 27 | 9 | 34 | 45 | 48 | 48 | 23 | 13 | 30 | 71 | | | |
| 27 | 25 | 27 | 35 | 19 | 33 | 31 | 35 | 26 | 41 | 44 | 39 | 38 | 32 | 20 | 33 | 54 | 44 | | |
| 31 | 20 | 13 | 24 | 12 | 19 | 18 | 21 | 12 | 31 | 46 | 45 | 47 | 24 | 16 | 27 | 41 | 40 | 36 | |

Figure ID. Similarity coefficients for kick samples taken during spring of 1985, Clark Fork River and tributaries (x 100). Coefficients greater than 40 are underlined; those greater than 60 are double-underlined. (Replicate data for each site combined.)

| Site Number | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 13 | 14 | 15 | 19 | 21 | 23 | 24 | 25 | 27 | 31 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | | | | | | | | | | | | | | | | |
| 2 | 38 | | | | | | | | | | | | | | | | | | |
| 4 | 58 | 44 | | | | | | | | | | | | | | | | | |
| 5 | 57 | 36 | 69 | | | | | | | | | | | | | | | | |
| 6 | 58 | 35 | 67 | 74 | | | | | | | | | | | | | | | |
| 8 | 54 | 31 | 69 | 73 | 75 | | | | | | | | | | | | | | |
| 9 | 48 | 33 | 61 | 56 | 68 | 70 | | | | | | | | | | | | | |
| 10 | 64 | 45 | 54 | 52 | 50 | 46 | 45 | | | | | | | | | | | | |
| 11 | 65 | 34 | 43 | 50 | 49 | 37 | 35 | 59 | | | | | | | | | | | |
| 13 | 62 | 36 | 47 | 50 | 61 | 50 | 55 | 56 | 61 | | | | | | | | | | |
| 14 | 36 | 23 | 28 | 29 | 47 | 32 | 49 | 35 | 41 | 62 | | | | | | | | | |
| 15 | 52 | 32 | 43 | 43 | 52 | 44 | 54 | 55 | 54 | 71 | 65 | | | | | | | | |
| 19 | 50 | 29 | 49 | 52 | 57 | 58 | 59 | 41 | 44 | 50 | 31 | 40 | | | | | | | |
| 21 | 31 | 29 | 48 | 44 | 52 | 51 | 54 | 36 | 29 | 38 | 37 | 39 | 61 | | | | | | |
| 23 | 10 | 13 | 10 | 9 | 13 | 10 | 12 | 11 | 9 | 13 | 21 | 17 | 11 | 22 | | | | | |
| 24 | 24 | 24 | 34 | 39 | 41 | 37 | 40 | 30 | 27 | 33 | 34 | 30 | 41 | 53 | 25 | | | | |
| 25 | 12 | 16 | 26 | 31 | 33 | 31 | 33 | 16 | 16 | 22 | 18 | 22 | 47 | 44 | 31 | 59 | | | |
| 27 | 9 | 18 | 11 | 9 | 9 | 5 | 11 | 14 | 10 | 13 | 12 | 15 | 9 | 13 | 16 | 18 | 17 | | |
| 31 | 9 | 7 | 7 | 4 | 13 | 10 | 17 | 8 | 7 | 14 | 32 | 20 | 8 | 21 | 35 | 31 | 25 | 10 | |

Figure IE. Similarity coefficients for kick samples taken during summer of 1985, Clark Fork River and tributaries (x 100). Coefficients greater than 40 are underlined; those greater than 60 are double-underlined. (Replicate data for each site combined.)

# APPENDIX III

# MASTER SPECIES LIST

MASTER SPECIES LIST - Species found in 1984-85 survey, Clark Fork River, Montana, and tributaries. U, M, or L under seasonal headings on right-hand side of page indicate species is one of five dominant taxa at one or more sites during that season in the upper (sites 1-9), middle (sites 11-21), or lower (sites 24-31) reaches, respectively, of the river.

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA | | | | | |
| EPHEMEROPTERA | | | | | |
| AMETROPODIDAE | | | | | |
| *Ametropus* sp. | | | | | |
| BAETIDAE | | | | | |
| *Baetis bicaudatus* | | | | | |
| *Baetis* poss. *flavistriga* | | | | | |
| *Baetis hageni* | | | | | |
| *Baetis insignificans* | | U,M | | | U,M |
| *Baetis tricaudatus* | U,M | U,M | U,M | U,M | U,M |
| *Centroptilum* sp. A | | M,L | | | |
| *Centroptilum* sp. B | | | | | |
| CAENIDAE | | | | | |
| *Caenis* prob. *simulans* | | | | | |
| EPHEMERELLIDAE | | | | | |
| *Attenella margarita* | | U,M,L | | | M |
| *Caudatella* poss. *hystrix* | | | | | |
| *Drunella doddsi* | | | | | |
| *Drunella* prob. *flavilinea* | | | | | |
| *Drunella grandis* | | | | | |
| *Ephemerella infrequens* | U,M | | U,M | U,M | |
| *Serratella tibialis* | | U | | | |
| *Timpanoga hecuba* | | | | | |
| EPHEMERIDAE | | | | | |
| *Hexagenia limbata* | | | | | |
| HEPTAGENIIDAE | | | | | |
| *Cinygmula* sp. | | | | | |
| *Epeorus albertae* | | | | | |
| *Heptagenia solitaria* | | | | | |
| *Nixe criddlei* | | | | | |
| *Nixe simplicioides* | | M,L | | | M |
| *Rhithrogena* poss. *hageni* | U,M | | U,M | U | M |
| *Stenonema* sp. | L | | L | L | L |

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| EPHEMEROPTERA (cont.) | | | | | |
| LEPTOPHLEBIIDAE | | | | | |
| *Leptophlebia* prob. *gravastella* | | | | | |
| *Paraleptophlebia bicornuta* | | | | | L |
| *Paraleptophlebia* poss. *debilis* | | | | | L |
| *Paraleptophlebia* poss. *memorialis* | M,L | | | | |
| *Paraleptophlebia* sp. A | | | | | |
| SIPHLONURIDAE | | | | | |
| *Ameletus* prob. *sparsatus* | | | | | |
| *Ameletus* prob. *velox* | | | | | |
| TRICORYTHIDAE | | | | | |
| *Tricorythodes minutus* | | U,M,L | | | U,M,L |
| PLECOPTERA | | | | | |
| CAPNIIDAE | | | | | |
| *Capnia*-group sp. | U | | | U,M | |
| CHLOROPERLIDAE | | | | | |
| *Alloperla*-group sp. | | | | | |
| NEMOURIDAE | | | | | |
| *Amphinemura* sp. | | | | | |
| *Malenka* sp. | | | | | |
| *Prostoia besametsa* | U | | | U | |
| *Zapada cinctipes* | | | | | |
| *Zapada columbiana* | | | | | |
| PERLIDAE | | | | | |
| *Calineuria californica* | | | | | |
| *Claassenia sabulosa* | | | | | |
| *Hesperoperla pacifica* | | | | | |
| PERLODIDAE | | | | | |
| *Cultus* poss. *pilatus* | U,M | | | | |
| *Isogenoides* poss. *elongatus* | U | U | | | |
| *Isoperla fulva* | U,M | | U | | |
| *Isoperla* prob. *quinquepunctata* | | | | | |
| *Skwala* prob. *parallela* | | | | | |
| PTERONARCYIDAE | | | | | |
| *Pteronarcella badia* | | U | | | |
| *Pteronarcys californica* | | | | | |
| TAENIOPTERYGIDAE | | | | | |
| *Taenionema* poss. *pacificum* | U | | | U | |

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| ODONATA | | | | | |
| AESHNIDAE | | | | | |
| *Aeshna* sp. | | | | | |
| GOMPHIDAE | | | | | |
| *Ophiogomphus* sp. | | | | | |
| COENAGRIONIDAE | | | | | |
| *Ischnura* sp. | | | | | |
| HEMIPTERA | | | | | |
| CORIXIDAE | | | | | |
| *Sigara* sp. | | | | | |
| *Rhagovelia* sp. | | | | | |
| TRICHOPTERA | | | | | |
| BRACHYCENTRIDAE | | | | | |
| *Brachycentrus americana* | | | | | |
| *Brachycentrus occidentalis* | | | | | |
| GLOSSOSOMATIDAE | | | | | |
| *Glossosoma* sp. | | | | | |
| *Protoptila* sp. | | | | | |
| HELICOPSYCHIDAE | | | | | |
| *Helicopsyche borealis* | | | | | |
| HYDROPSYCHIDAE | | | | | |
| *Arctopsyche grandis* | | U | | | |
| *Cheumatopsyche* sp. | U,L | U,M,L | U,M,L | U,M | U,M,L |
| *Hydropsyche* sp. A | | | | | |
| *Hydropsyche* poss. *occidentalis* | | M | U,M,L | U | U,M |
| *Symphitopsyche* poss. *cockerelli* | U,L | U,M | U | | U,M |
| *Symphitopsyche* poss. *slossonae* | | | | | |
| HYDROPTILIDAE | | | | | |
| *Hydroptila* sp. | U,M | M | U,M | M,L | M |
| *Leucotrichia* prob. *pictipes* | | | | | |
| *Neotrichia* sp. | | | | | |
| *Oxyethira* sp. | | | | | |
| *Zumatrichia notosa* | | | | | |
| LEPIDOSTOMATIDAE | | | | | |
| *Lepidostoma* sp. | | | | | |
| LEPTOCERDIAE | | | | | |
| *Ceraclea* sp. | | | L | | |
| *Mystacides* sp. | | | | | |
| *Nectopsyche* sp. | | | | | |

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| TRICHOPTERA (cont.) | | | | | |
| LEPTOCERIDAE (cont.) | | | | | |
| *Oecetis* sp. A | | | U | | |
| *Oecetis* sp. B | | | | | |
| *Triaenodes* sp. | | | | | |
| LIMNEPHILIDAE | | | | | |
| *Apatania* sp. | | | | | |
| *Dicosmoecus* sp. | | | | | |
| *Onocosmoecus* sp. | | | | | |
| PHILOPOTAMIDAE | | | | | |
| *Wormaldia* sp. | | | | | |
| POLYCENTROPODIDAE | | | | | |
| *Polycentropus* sp. | | | | | |
| PSYCHOMYIIDAE | | | | | |
| *Psychomyia flavida* | | | | U | |
| RHYACOPHILIDAE | | | | | |
| *Rhyacophila angelita* | | | | | |
| *Rhyacophila* prob. *bifila* | | | | | |
| LEPIDOPTERA | | | | | |
| PYRALIDAE | | | | | |
| *Parargyractis* sp. | | | | | |
| COLEOPTERA | | | | | |
| DYTISCIDAE | | | | | |
| *Oreodytes scitilus* | | | | | |
| ELMIDAE | | | | | |
| *Dubiraphia* sp. | | | | | |
| *Narpus concolor* | | | | | |
| *Optioservus divergens/quadrimaculatus* | | | | | |
| *Stenelmis* sp. | | | | | |
| *Zaitzevia parvula* | | | | | L |
| GYRINIDAE | | | | | |
| *Gyrinus* sp. | | | | | |
| HALIPLIDAE | | | | | |
| *Brychius* sp. | | | | | |
| HYDROPHILIDAE | | | | | |
| *Anacaena* sp. | | | | | |
| *Helophorus* sp. | | | | | |
| *Hydrochus* sp. | | | | | |

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| DIPTERA | | | | | |
| ATHERICIDAE | | | | | |
| *Atherix variegata* | | | | | |
| CERATOPOGONIDAE | | | | | |
| *Palpomyia*-group sp. A | | | | | |
| *Palpomyia*-group sp. B | | | | | |
| CHIRONOMIDAE | | | | | |
| CHIRONOMINAE | | | | | |
| *Chironomus* sp. | | | | | |
| *Cladotanytarsus* sp. A | | | | | |
| *Cladotanytarsus* sp. B | | | | | |
| *Cryptochironomus* sp. | | | | | |
| *Cryptotendipes* sp. | | | | | |
| *Dicrotendipes* sp. A | | | | | |
| *Dicrotendipes* sp. B | L | | | | L |
| *Dicrotendipes* sp. C | | | | | |
| *Harnischia* sp. | | | | | |
| *Lenziella* sp. | | | | | |
| *Micropsectra* sp. A | | | | L | |
| *Micropsectra* sp. B | | | | | |
| *Micropsectra* sp. C* | | | | | |
| *Microtendipes* sp. | | M,L | U,M,L | | M,L |
| *Pagastiella* sp.** | | | | | |
| *Parachironomus* sp. | | L | | | |
| *Parachironomus* sp. B | | | | | |
| *Paracladopelma* sp. A | | | | | |
| *Paracladopelma* sp. B | | | | | |
| *Paracladopelma* sp. C | | | | | |
| *Paralauterborniella* sp. | | | | | |
| *Paratanytarsus* sp. | | | | | |
| *Paratanytarsus* sp. B | | | | | |
| *Phaenopsectra* sp. | | | | | |
| *Phaenopsectra* sp. B | | | | | |
| *Polypedilum* sp. A | | U | | | U,M |
| *Polypedilum* sp. B | | | | | |
| *Polypedilum* sp. C | | | | | |
| *Polypedilum* sp. D | | | | | |

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*Same as *Tanytarsus* sp. B.

**Same as *Paralauterborniella* sp.

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| DIPTERA (cont.) | | | | | |
| CHIRONOMIDAE (cont.) | | | | | |
| CHIRONOMINAE (cont.) | | | | | |
| *Pseudochironomus* sp. | | | | | |
| *Rheotanytarsus* sp. | | | | | |
| *Robackia* sp. | | | | | |
| *Stempellina* sp. | | | | | |
| *Stempellinella* sp. | | | | | |
| *Stenochironomus* sp. | | | | | |
| *Stictochironomus* sp. | | | | | |
| *Tanytarsus* sp. A | | | | | |
| *Tanytarsus* sp. B | | | | U | L |
| *Tanytarsus* sp. C | | | | | |
| *Xenochironomus* sp. | | | | | |
| DIAMESINAE | | | | | |
| *Diamesa* sp. A | | | | | |
| *Diamesa* sp. B | | | | | |
| *Diamesa* sp. C | | | | | |
| *Pagastia* sp. | L | | | | |
| *Potthastia* sp. | | | | | |
| *Sympotthastia* sp. | | | | | |
| PRODIAMESINAE | | | | | |
| *Monodiamesa* sp. | | | | | |
| *Odontomesa* sp. | | | | | |
| ORTHOCLADIINAE | | | | | |
| *Brillia* sp. | | | | | |
| *Cardiocladius* sp. | | | | | |
| *Cardiocladius* sp. B | | | | | |
| *Cardiocladius* sp. C | | | | | |
| *Corynoneura* sp. | | | | | |
| *Cricotopus* sp. A* | | | | | |
| *Cricotopus* sp. B | M | | L | U,M,L | |
| *Cricotopus* sp. C | | | | | |
| *Cricotopus* sp. D | | | | | |
| *Cricotopus* sp. E | | | | | |
| *Eukiefferiella* sp. A | | | | L | |
| *Eukiefferiella* sp. B | | | | | |
| *Eukiefferiella* sp. C | | | | | |

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*Same as *Orthocladius* sp. B.

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| DIPTERA (cont.) | | | | | |
| CHIRONOMIDAE (cont.) | | | | | |
| ORTHOCLADIINAE (cont.) | | | | | |
| *Eukiefferiella* sp. D | | | | | |
| *Eukiefferiella* sp. E | | | | | L |
| *Eukiefferiella* sp. F | | | | | |
| *Eukiefferiella* sp. G | | | | | |
| *Eukiefferiella* sp. H | | | | | |
| *Eukiefferiella* sp. I | | | | | |
| *Heterotrissocladius* sp. | | | | | |
| *Orthocladius* (*Euorthocladius*) sp. | M,L | | | U,M,L | |
| *Orthocladius* sp. A | | | | | |
| *Orthocladius* sp. B | | | | U,M | |
| *Orthocladius* sp. C | | | | | |
| *Orthocladius* sp. D | | | | | |
| *Orthocladius* sp. E | | | | | |
| *Orthocladius* sp. F | | | | | |
| *Orthocladius* sp. G | | | | | |
| *Orthocladius* poss. *mallochi* | | | | | |
| *Orthocladius* poss. *nigritus* | | | | | |
| *Orthocladius* poss. *obumbratus* | L | | M | U,M,L | M,L |
| *Parametriocnemus* sp. | | | | | |
| *Psectrocladius* sp. A | | | | | |
| *Psectrocladius* sp. B | | | | | |
| *Psectrocladius* sp. C | | | | | |
| *Synorthocladius* sp. | | | | | |
| *Thienemaniella* sp. | | | | | |
| *Trissocladius* sp. | L | | | | |
| TANYPODINAE | | | | | |
| *Thienemannimyia*-group sp. | | | | | |
| *Procladius* sp. A | | | | | |
| *Procladius* sp. B | | | | | |
| DOLICHOPODIDAE | | | | | |
| EMPIDIDAE | | | | | |
| *Chelifera* sp. | | | | | |
| *Wiedemannia* sp. | | | | | |
| EPHYDRIDAE | | | | | |

*Misidentified as *Ablabesmyia* sp. in raw data.

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| INSECTA (cont.) | | | | | |
| DIPTERA (cont.) | | | | | |
| SIMULIIDAE | | | | | |
| *Prosimulium* sp. | | | | | |
| *Simulium* sp. | M | | L | U,M,L | M |
| TABANIDAE | | | | | |
| *Chrysops* sp. | | | | | |
| TANYDERIDAE | | | | | |
| *Protanyderus* sp. | | | | | |
| TIPULIDAE | | | | | |
| *Antocha* sp. | | | | | |
| *Hexatoma* sp. | | | | | |
| *Ormosia* sp. | | | | | |
| *Tipula* sp. | | | | | |
| CLADOCERA | | | | | L |
| COPEPODA | | | | | |
| OSTRACODA | | | | | |
| AMPHIPODA | | | | | |
| GAMMARIDAE | | | | | |
| *Gammarus* sp. | | | | | |
| TALITRIDAE | | | | | |
| *Hyalella azteca* | | | | | |
| DECAPODA | | | | | |
| ASTACIDAE | | | | | |
| *Pacifasticus* sp. | | | | | |
| HYDRACARINA | | | | | |
| ARRENURIDAE | | | | | |
| *Arrenurus* sp. | | | | | |
| LEBERTIIDAE | | | | | |
| *Lebertia* sp. | | | | | |
| SPERCHONIDAE | | | | | |
| *Sperchon* sp. | | | | | |
| UNIONICOLIDAE | | | | | |
| *Unionicola* sp. | | | | | |
| GASTROPODA | | | | | |
| ANCYLIDAE | | | | | |
| *Ferrissia* sp. | | | | | |
| PLANORBIDAE | | | | | |
| Gyraulus sp. | | | | L | L |
| LYMNAEIDAE | | | | | |
| Lymnaea sp. | | | L | | L |

| Species | Spring 1984 | Summer 1984 | Fall 1984 | Spring 1985 | Summer 1985 |
|---|---|---|---|---|---|
| GASTROPODA (cont.) | | | | | |
| PHYSIDAE | | | | | |
| *Physa* sp. | | | | | |
| PELECYPODA | | | | | |
| SPHAERIIDAE | | | | | |
| *Pisidium* sp. | | | | | |
| OLIGOCHAETA | | | | | |
| [unidentified] | | U,L | | U | |
| LUMBRICIDAE | | L | | | L |
| HIRUDINEA | | | | | |
| [unidentified] | | | | | |
| ERPOBDELLIDAE | | | | | |
| *Dina* sp. | | | | | |
| GLOSSIPHONIIDAE | | | | | |
| *Glossiphonia* sp. | | | | | |
| *Helobdella* sp. | | | | | |
| TURBELLARIA | | | | | |
| GORDIOIDEA | | | | | |

pendix IV

## Lower Clark Fork River Study Monitoring Station Descriptions.*

### A. Shallow-water Monitoring Stations

| Station Number | Station Name | Legal Description | River Mile | Average Annual Flow (cfs) | Station Rationale |
|---|---|---|---|---|---|
| 01 | Clark Fork at Turah | T12N R18W Sec. 01 CBC | 0.0 | 1712 | Control station above Milltown Reservoir. Known metals problem from historic mining and smelting activities in headwaters. |
| 02 | Blackfoot River near mouth | T13N R17W Sec. 09 BDD | 6.0 | 1645 | Major tributary to the Clark Fork and a control station above Milltown Reservoir. |
| 03 | Clark Fork in Milltown Reservoir | T13N R18W Sec. 20 DAA | 6.0 | — | Milltown Reservoir is a designated Superfund site and has trapped large quantities of metals originating upstream in the Clark Fork drainage. |
| 04 | Clark Fork below Milltown Dam | T13N R18W Sec. 18 CBC | 8.5 | 3051 | Station allows comparison of metals and other pollutants from above to below reservoir. |
| 05 | Clark Fork above Missoula | T13N R19W Sec. 22 DDD | 12.5 | 3051 | Control station above City of Missoula. |
| 06 | Clark Fork above Missoula wastewater treatment plant (WWTP) | T13N R19W Sec. 18 DDA | 15.9 | 3161 (Est.) | Station allows examination of effects of City of Missoula on Clark Fork water quality. |
| 07 | Missoula WWTP discharge to Clark Fork | T13N R19W Sec. 18 DDA | 16.0 | 8.9* | Large volume point source municipal discharge to Clark Fork. |
| 08 | Clark Fork just below Missoula WWTP discharge | T13N R19W Sec. 18 DDD | 16.1 | 3170 (Est.) | Station located in the plume of the WWTP discharge prior to complete mixing. Worst-case situation. |
| 09 | Clark Fork at Shuffield's (Schmidt Construction Co.) | T13N R20W Sec. 24 AAD | 18.0 | 3170 (Est.) | Station allows examination of effects of Missoula WWTP after complete mixing. |
| 10 | Bitterroot River near mouth | T13N R20W Sec. 26 CBD | 21.0 | 2377 (Est.) | Major tributary to the Clark Fork. |
| 11 | Clark Fork at Harper's Bridge | T14N R21W Sec. 35 ADA | 28.5 | 5547 | Control station above Champion Frenchtown Mill. |
| 12 | Champion International Frenchtown Mill wastewater surface discharge<br>Discharge 001<br>Discharge 002 | T14N R21W Sec. 23 DBB<br>T14N R21W Sec. 14 BBC | 31.0<br>32.0 | 9.2 (Averaged combined flow)* | Large volume point source industrial discharge to Clark Fork and the primary focal point of this study. |

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*Provided by Montana DHES staff.

| Station Number | Station Name | Legal Description | River Mile | Average Annual Flow (cfs) | Station Rationale |
|---|---|---|---|---|---|
| 13 | Clark Fork at Marcure (0.5 miles below Champion surface discharge) | T14N R21W Sec. 11 BCB | 32.5 | 5560 (Est.) | Worst-case situation (mixing incomplete) below Champion surface discharge, rapid infiltration basins and storage ponds seepage areas. |
| 14 | Clark Fork near Frenchtown (4 miles below Champion surface discharge) | T14N R21W Sec. 03 BA | 36.0 | 5560 (Est.) | Station located below additional seepage areas. Mixing of surface discharge well underway. |
| 15 | Clark Fork at Huson** | | | 5560 (Est.) | Station where routine Champion self-monitoring and State compliance monitoring is performed. Surface discharge and seepage well-mixed. |
| | Shefer Ranch | T15N R22W Sec. 36 BBB | 39.0 | | |
| | Sixmile Station | T15N R22W Sec. 26 ACB | 40.5 | | |
| 16 | Clark Fork at Ninemile | T15N R22W Sec. 32 DBB | 46.0 | — | Stations 16-21 allow examination of the effects of the Missoula WWTP and Champion discharges and other pollutants (e.g. metals) with increasing distance from their sources. They also allow the identification of any new significant water quality contaminant sources. |
| 17 | Clark Fork near Alberton | T14N R23W Sec. 12 AAB | 51.0 | — | |
| 18 | Clark Fork at Tarkio | T15N R25W Sec. 34 ADC | 70.0 | — | |
| 19 | Clark Fork at Lozeau | T16N R25W Sec. 29 DBA | 79.0 | — | |
| 20 | Clark Fork at Superior | T17N R26W Sec. 34 ABB | 89.0 | — | |
| 21 | Clark Fork near St. Regis | T18N R27W Sec. 09 CCC | 105.0 | 7580 | |
| 22 | Clark Fork above Flathead River confluence | T19N R25W Sec. 33 DAD | 128.5 | 7580 | Control station for Clark Fork water quality above Flathead River. |
| 23 | Flathead River near mouth | T18N R24W Sec. 05 DDC | 129.0 | 12400 | Major tributary to the the Clark Fork. |
| 24 | Clark Fork at Plains | T20N R26W Sec. 34 ABB | 138.0 | 19980 | Station allows examination of Clark Fork water quality after mixing with Flathead River. |
| 25 | Clark Fork above Thompson Falls Reservoir | T21N R27W Sec. 33 BCB | 153.0 | 19980 | Control station above Thompson Falls Reservoir. |
| 26 | Clark Fork in Thompson Falls Reservoir | T21N R29W Sec. 08 BCC | 169.0 | — | Station allows examination of changes in Clark Fork water quality as it passes through the reservoir. |

| Station Number | Station Name | Legal Description | River Mile | Average Annual Flow (cfs) | Station Rationale |
|---|---|---|---|---|---|
| 27 | Clark Fork below Thompson Falls Dam | T22N R30W Sec. 36 BDC | 173.0 | 20702 | Station allows comparison of water quality from above to below the reservoir. It also serves as a control station above Noxon Rapids Reservoir. |
| 28 | Clark Fork in Noxon Rapids Reservoir | T24N R32W Sec. 01 DDD | 198.0 | — | Same rationale as for 26 above. |
| 29 | Clark Fork below Noxon Rapids Dam*** | | | 21220 | Station allows comparison of water quality from above to below reservoir and acts as a control station above Cabinet Gorge Reservoir. |
| | Above Rock Creek | T26N R32W Sec. 32 AAC | 209.0 | | |
| | At Noxon Bridge | T26N R32W Sec. 19 DAB | 210.0 | | |
| 30 | Clark Fork in Cabinet Gorge Reservoir | T27N R34W Sec. 28 DDB | 224.0 | — | Same rationale as for 26 above. |
| 31 | Clark Fork below Cabinet Gorge Dam | T27N R3E Sec. 20 DCC | 232.0 | 22410 | Station allows comparison of water quality from above to below Cabinet Gorge Reservoir. It also indicates quality of Clark Fork as it enters Lake Pend Oreille. Station is monitored by both Montana and Idaho and serves as a check on each state's data quality. |

* Average flow rates for Missoula WWTP and Champion discharges are averages for the period July 1984 - June 1985.

** Shefer Ranch station sampled during seasonal comprehensive monitoring runs. Routine water chemistry monitoring conducted at Sixmile Station because of easier access.

*** Station above Rock Creek sampled through 1984. Station relocated downstream to Noxon Bridge in 1985 to provide baseline data for proposed developments in the Rock Creek drainage.

B. Deep-water Monitoring Stations

| Station Number | Station Name | Legal Description | River Mile | Average Annual Flow (cfs) | Station Rationale |
|---|---|---|---|---|---|
| 03 | Clark Fork arm of Milltown Reservoir | T13N R18W Sec. 21 CA | 6.0 | — | High concentrations of metals in bottom sediments. |
| 13 | Clark Fork - Marcure Pool | T14N R21W Sec. 3 DB | 32.5 | — | Stations 13-22 are located between the Champion Frenchtown Mill and the Flathead River confluence. These stations were established to examine whether there is appreciable settling of organic solids from the Missoula WWTP and Champion discharges in deep river pools and whether such deposition affects Clark Fork water quality. A second objective was to investigate the fate of metal-bearing sediments originating upstream and their subsequent effects. |
| 15 | Clark Fork - Huson Pool | T15N R22W Sec. 26 DC | 40.0 | — | |
| 16 | Clark Fork - Ninemile Pool | T15N R22W Sec. 32 ACC | 46.0 | — | |
| 17 | Clark Fork - Fish Creek Pool | T14N R25W Sec. 1 C | 69.5 | — | |
| 18 | Clark Fork - Tarkio Pool | T15N R25W Sec. 27 B | 71.0 | — | |
| 19.5 | Clark Fork - Superior Pool | T16N R25W Sec. 13 CD | 85.0 | — | |
| 20 | Clark Fork - LaVista Pool | T17N R27W Sec. 19 D | 91.5 | — | |
| 20.5 | Clark Fork - Red Hill Pool | T17N R27W Sec. 5 BB | 100.0 | — | |
| 21 | Clark Fork - Boxcar Pool | T18N R27W Sec. 20 AC | 105.0 | — | |
| 21.5 | Clark Fork - Toole Pool | T18N R27W Sec. 10 DC | 107.0 | — | |
| 22 | Clark Fork - Flathead Pool | T18N R25W Sec. 9 AA | 123.0 | — | |
| 26 | Thompson Falls Reservoir | | | — | Deep water reservoir stations were selected to examine fate and effects of metals and organic solids originating upstream and which may have deposited in the reservoirs. A second objective was to examine oxygen depletion due to reservoir stratification. |
| | Near boat dock | T21N R29W Sec. 8 DB | 169.0 | | |
| | Below sawmill | T21N R29W Sec. 9 CBC | 169.0 | | |
| 28 | Noxon Rapids Reservoir | | | — | |
| | Near Trout Creek | T24N R31W Sec. 16 BC | 198.0 | | |
| | North Shore Campground | T24N R32W Sec. 12 AAD | 200.0 | | |
| 30 | Cabinet Gorge Reservoir | | | — | |
| | Near Bull River | T26N R33W Sec. 9 DA | 225.0 | | |
| | Near Heron | T27N R34W Sec. 26 DC | 230.0 | | |

# G. CRAYFISH METALS STUDY

# Evaluation of copper concentrations in crayfish (Pacification trowbridgi) from various segments of the Clark Fork River drainage, Montana

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# INTRODUCTION

During the evaluation of Champion International Corporation's request for a year around discharge permit, it was argued that oxygen demanding materials could cause reducing conditions to develop at the sediment-water interface which in turn could increase the mobility and subsequent bioavailability of metals present in the sediments. It was further argued that these conditions might exist only in or on the surface of the substrate and would therefore not be apparent from measurements of dissolved oxygen in the water column.

To evaluate the above, we collected pacific crayfish (Pacifastacus trowbridgi) from several locations in the Clark Fork River drainage including locations both upstream of and downstream from the pulp mill; copper concentrations were determined in selected tissues including exoskeleton, hepatopancreas, and gill.

We reasoned that crayfish were an appropriate subject for this evaluation because they have a relatively small home range (hence migration is not a problem) and they tend to inhabit areas of low current velocity where deposition of both organic material and metals rich suspended solids would be expected.

Copper was chosen over other metals because previous work (Phillips 1985) has demonstrated that copper is present in the Clark Fork River at higher concentrations than other metals relative to its toxicity. Data collected in the Clark Fork River upstream of its confluence with Rock Creek suggest the copper is limiting fish populations in that portion of the river.

# METHODS

## Sampling

Crayfish were collected from several locations in the mainstem of the Clark Fork River and from one location in the Bitterroot River (Fig. 1); the latter served as a control. Collection occurred from September 10-14, 1984. Sampling sites included downstream of Milltown Dam, downstream of Missoula but upstream of the confluence with the Bitterroot River, downstream of the pulp mill outfall, near Superior, downstream of the confluence with the Flathead River, downstream of Thompson Falls Dam, and downstream of Noxon Dam. Late summer sampling was preferred because we wanted to sample crayfish following the season of higher water temperatures and lower dissolved oxygen concentrations and after the first year of summer discharge by the Champion International Mill. We also wanted to collect crayfish well after their spring molting but prior to the time when they molt in the fall.

Crayfish were captured in baited traps constructed with two inch funnel openings at each end. Traps were submerged in likely crayfish habitat, fished overnight, and retrieved the following day. Sample sizes ranged from seven to ten crayfish per site. So as not to introduce bias, we discarded crayfish that had just completed molting.

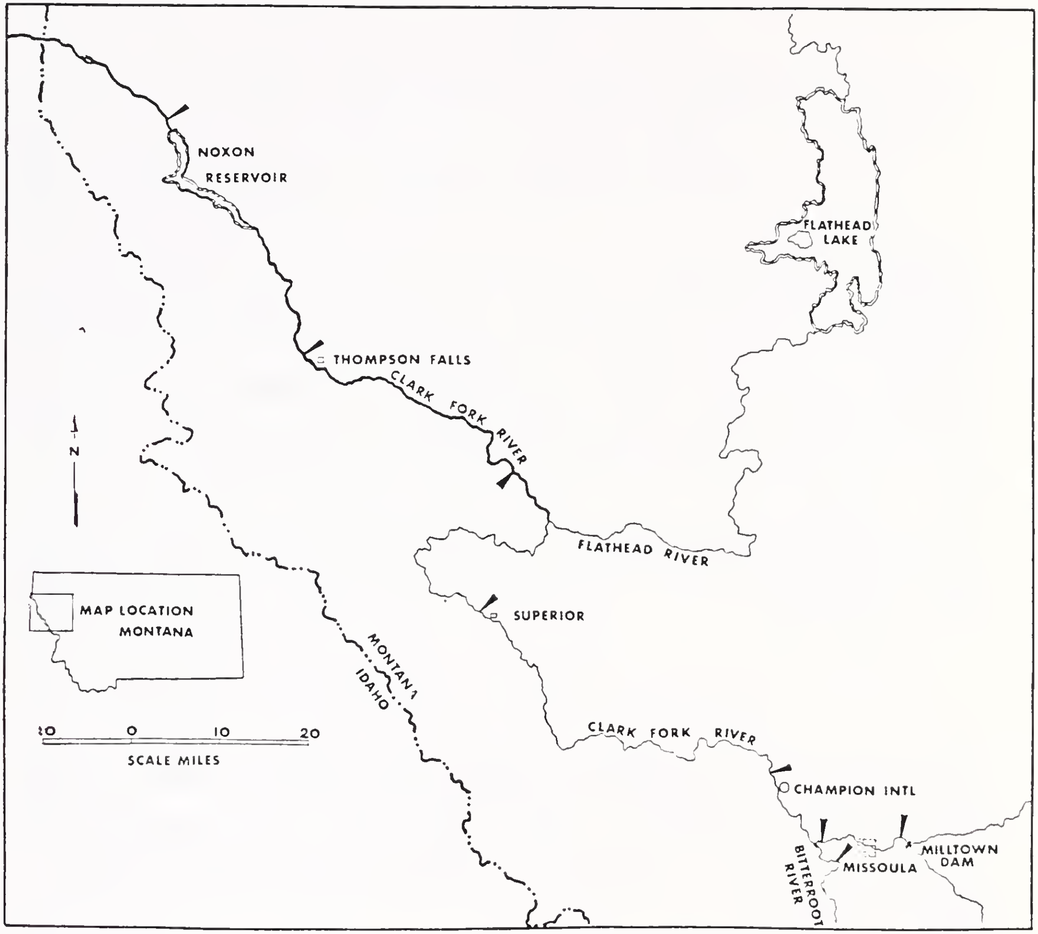

Figure 1. Map of the Clark Fork River showing locations where crayfish were sampled (indicated by arrows).

## Analytical

Tissues analyzed for copper included exoskeleton, hepatopancreas and gill. A few samples were also analyzed for cadmium; however, accuracy checks using National Bureau of Standards bovine liver indicated that the level of error was unacceptable; cadmium was therefore dropped from further consideration.

Tissues were dissected, freeze dried, ground, homogenized and digested in nitric acid prior to analysis by atomic absorption spectrophotometry (Van Meter 1974). The instrument used was a Varian AA 275 BD unit and the detection limit for copper was approximately 0.7 ug/g. Analytical work was contracted to the Gordon Environmental Studies Laboratory, University of Montana.

Quality control measures included recovery of spiked samples, analysis of National Bureau of Standards reference materials, and analysis of duplicate samples (both from separate digestions of the same tissue and replicate analysis of material from the same digestion). The poorest result for any of the quality control measures for copper in tissue was 18% variation between duplicate digestions of one of the reference materials. In the majority of cases, however, checks on accuracy indicated that the error was inside of 10%. We judged, therefore, that the results for copper were acceptable.

## Statistics

Duncan's multiple range test was used to compare sample means for both crayfish length and copper in exoskeleton for each of the various locations (Steel and Torrie 1960). Linear regression analysis was employed to determine, at a given location, the relationship between copper in exoskeleton and crayfish length.

# RESULTS

From two of the locations, below Noxon and Milltown Dams, copper was determined in gill and hepatopancreas as well as in exoskeleton (Table 1). Copper concentrations were more than an order of magnitude higher in gill and hepatopancreas than in exoskeleton. These high concentrations are probably owing to the fact that copper is a normal constituent in the hemolymph of crayfish, playing a role similar to iron in mammalian hemoglobin. Copper may be internally regulated by highly vascularized organs. Consequently, gill and hepatopancreas of crayfish may not be appropriate tissues for gauging ambient copper concentrations in the environment. Exoskeleton was judged to be the tissue that best fit the needs of this assessment.

Crayfish collected below Milltown Dam were significantly smaller ($p < 0.05$) than those collected from several other locations including near Superior, downstream of the pulp mill, and below the confluence with the Flathead River (Table 2). We were concerned that size differences could bias comparisons between locations because many bioaccumulative chemicals tend to increase in concentration with size and age of the organisms.

Accordingly, we evaluated the relationship between crayfish length and copper in exoskeleton for each of the sampling locations using linear regression analysis (Table 3).

In all instances the correlation between copper in exoskeleton and crayfish length was poor; at five of the eight locations the coefficient of determination

Table 1. A comparison of copper concentrations (dry weight) in various tissues of crayfish collected from the Clark Fork River.

| Location | Tissue | n | Copper ug/g (dry basis) Mean | Range | SD |
|---|---|---|---|---|---|
| Clark Fork, below Noxon Dam | Gill | 5 | 424 | 284-560 | 115 |
| | Hepatopancreas | 5 | 495 | 214-734 | 201 |
| | Exoskeleton | 10 | 26 | 12-53 | 14 |
| Clark Fork, below Milltown Dam | Gill | 5 | 388 | 351-421 | 25 |
| | Hepatopancreas | 5 | 484 | 372-652 | 85 |
| | Exoskeleton | 10 | 34 | 23-46 | 8 |

Table 2. Lengths of crayfish collected from the Clark Fork drainage, September 10-14, 1984.

| Location<br>and<br>(sample size) | Crayfish total length (in.)<br>Mean ± SD | <br>Range | Grouping[a] | |
|---|---|---|---|---|
| Clark Fork, near Superior (9) | 4.3 ± 0.4 | 3.6-4.9 | | ┐ |
| Clark Fork, below Champion (10) | 4.2 ± 0.3 | 3.8-4.7 | | │ |
| Clark Fork, below Flathead River (7) | 4.2 ± 0.5 | 3.6-4.8 | | │ |
| Bitterroot River, control (10) | 4.1 ± 0.3 | 3.5-4.4 | ┐ | │ |
| Clark Fork River, near Missoula (8) | 4.0 ± 0.5 | 3.5-4.9 | │ | │ |
| Clark Fork, below Noxon (8) | 4.0 ± 0.6 | 2.8-4.7 | │ | │ |
| Clark Fork, below Thompson Falls (8) | 3.8 ± 0.6 | 3.0-4.9 | │ | ┘ |
| Clark Fork, below Milltown (10) | 3.6 ± 0.5 | 3.1-4.5 | ┘ | |

[a] Means within the same line are not significantly different from each other (95% confidence level) according to Duncan's Multiple Range Test.

Table 3. Regression equations and coefficients of determination showing the poor correlation between crayfish length and copper in exoskeleton for several locations in the Clark Fork River drainage.

| Location and (sample size) | Regression (Copper = a length -b) | Coefficient of determination ($r^2$) |
|---|---|---|
| Bitterroot River - control (10) | y = -22x+104 | 0.47 |
| Clark Fork, near Missoula (10) | y = -4x+40 | 0.08 |
| Clark Fork, near Superior (10) | y = 10x-21 | 0.10 |
| Clark Fork, below Flathead River (8) | y = -31x+173 | 0.36 |
| Clark Fork, below Milltown Dam (10) | y = -3x+46 | 0.04 |
| Clark Fork, below Champion (10) | y = -3x+35 | 0.03 |
| Clark Fork, below Thompson Falls (9) | y = 6x+18 | 0.02 |
| Clark Fork, below Noxon Dam (8) | y = -15x+86 | 0.45 |

was 0.10 or less. We therefore conclude that differences in lengths of crayfish collected from the various locations did not bias our comparison between sites of copper in exoskeletons.

Crayfish from the Bitterroot River, the control station, had the lowest copper concentrations in exoskeleton of all the locations sampled (Table 4). They were, however, statistically different ($p < 0.05$) only from the three locations where crayfish contained the highest concentrations of copper. Diffuse tailings deposits located throughout the upper Clark Fork watershed frequently cause high copper concentrations in Clark Fork River water, particularly during periods of high river discharge (Phillips 1985). Exceedences of criteria for the protection of freshwater aquatic life have been documented in the Clark Fork River as far downstream as Thompson Falls (Water Quality Bureau, unpublished data). Comparatively, copper is seldom present in Bitterroot River Water at concentrations above the analytical detection limit for copper (Water Quality Bureau, unpublished data). Lower copper concentrations in crayfish from the Bitterroot River compared to the Clark Fork River is consistent with water quality data.

Highest copper concentrations were in crayfish collected downstream of: (1) Milltown Dam, (2) the confluence with the Flathead River, and (3) Thompson Falls Dam. In the case of the latter two locations, copper concentrations were statistically higher ($p < 0.05$) than from all other locations sampled (Table 4),

Higher concentrations at locations downstream of the Flathead River may be related to higher water temperatures and lower oxygen concentrations that occur over that river reach. These conditions tend to increase the solubility of

Table 4. Copper concentrations in exoskeletons of crayfish collected from the Clark Fork River drainage, September 10-14, 1984.

| Location and (sample size) | Copper ug/g (dry basis) | | Groupings[a] |
|---|---|---|---|
| | Mean ±SD | Range | |
| Bitterroot River - control (10) | 16±9 | 9-39 | |
| Clark Fork, below Champion (10) | 22±6 | 14-34 | |
| Clark Fork, near Superior (9) | 23±13 | 8-54 | |
| Clark Fork, near Missoula (8) | 24±6 | 14-33 | |
| Clark Fork, below Noxon Dam (8) | 26±14 | 12-53 | |
| Clark Fork, below Milltown Dam (10) | 34±8 | 23-46 | |
| Clark Fork, below Flathead River (7) | 41±25 | 14-72 | |
| Clark Fork, near Thompson Falls (8) | 42±24 | 17-85 | |

[a] Means within the same line are not significantly different from each other (95% confidence level) according to Duncan's Multiple Range Test.

metals and also the metabolic rates, and hence, exposure to metals by organisms living in water. Although higher water temperatures and low oxygen concentrations persist downstream of Noxon Reservoir, copper concentrations tend to be lower below the dam than upstream (Water Quality Bureau, unpublished data). This may explain the lower concentrations of copper in crayfish from below Noxon Dam and suggests that the reservoir is acting as a sink for copper.

Clearly, our interpretation of the data is limited by relatively small sample sizes and a somewhat cursory understanding of water quality and physical habitat parameters at each of the locations where crayfish were sampled. Nonetheless, no statistically significant differences ($p < 0.05$) were seen in crayfish collected immediately upstream from and downstream of the pulp mill. The data do not support the hypothesis that the Champion International discharge is an important factor in the mobilization of copper and its subsequent accumulation by crayfish. Silverman and Gordon (1983) were also unable to find evidence that the pulp mill affects metals accumulation by crayfish.

## SUMMARY

1. Copper concentrations were much higher in the gills and hepatopancreas of crayfish than in exoskeleton. Copper is a normal constituent of the hemolymph of crayfish, playing a role similar to iron in mammalian hemoglobin. Because of this, copper is naturally elevated in highly vascularized tissues such as gill and hepatopancreas. Consequently, these tissues are probably not appropriate for this type of monitoring.

2. Crayfish collected below Milltown Dam were significantly shorter than crayfish from three downstream sampling locations (near Superior and below Champion and the Flathead River). However, crayfish length was poorly correlated with copper in exoskeleton for any given location, consequently differences in crayfish lengths between locations should not bias comparison of mean copper concentrations in exoskeleton.

3. Exoskeletons of crayfish collected below Milltown Dam contained higher copper concentrations than crayfish from all locations except below the Flathead River and near Thompson Falls. However, the difference was statistically significant only in the case of the Bitterroot. The lowest average copper concentrations were in crayfish from the Bitterroot River (the control); however, these were not significantly lower than in crayfish from other locations including below Champion and Noxon Dam, and near Missoula and Superior.

4. Copper concentrations were significantly higher in exoskeletons of crayfish collected in the Clark Fork downstream of the Flathead River and near Thompson Falls than at all other locations sampled except below Milltown Dam. Several factors may be involved. Copper concentrations in Clark Fork River water tend to gradually decrease as you move downstream from Milltown Dam. However, the Flathead River is warmer than the Clark Fork hence the Clark Fork is warmer downstream of its confluence with the Flathead. Higher water temperatures increase the solubility of metals and the metabolic rates of organisms living in water. Additionally, the Flathead River experiences lower oxygen sags than the Clark Fork, hence minimum oxygen concentrations are lower in the Clark Fork downstream of the Flathead River than upstream. Lowered oxygen concentrations increase the respiration rates or organisms living in water and thereby increase their exposure to chemicals present in water.

5. Below Noxon Dam, copper concentrations in crayfish return to the lower concentrations found in crayfish upstream from the confluence with the Flathead River. Water temperatures continue to be higher and dissolved oxygen concentrations lower downstream of Noxon Dam but Water Quality Bureau data show that copper was never present at detectable levels below Noxon. Noxon Reservoir is probably a sink for copper.

6. No statistically significant differences were seen in copper present in crayfish collected immediately upstream from and downstream of the pulp mill. The data do not support the hypothesis that the Champion International discharge is an important factor in mobilization of copper and its subsequent accumulation by crayfish.

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# H. RESERVOIR SEDIMENT STUDY

NOTE: This paper will be published in the proceedings of the Clark Fork River Symposium, January 1986.

# COPPER, ZINC, AND ARSENIC IN BOTTOM SEDIMENTS OF CLARK FORK RIVER RESERVOIRS--PRELIMINARY FINDINGS

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Abstract--Acetic acid extracts of sediments from four Clark Fork River reservoirs,--Milltown, Thompson Falls, Noxon Rapids, and Cabinet Gorge--indicate that mining and smelting operations in the upper drainage have enriched metal concentrations throughout the river. Milltown Reservoir contains metal values over 10 times the background levels for copper, zinc, and arsenic. Enrichment over background decreases downstream where the lower reservoirs contain copper and zinc concentrations 4 to 10 times over background values. In the lower reservoirs arsenic is not elevated over background. These trends suggest that contaminants have been transported over 350 miles from the major source of metals in the upper drainage and very likely reside in the sediments of the Clark Fork River delta in Lake Pend Oreille.

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## INTRODUCTION

The Clark Fork River originates in the Anaconda-Butte region from the confluence of Silver Bow Creek, Mill Creek, Willow Creek, and Warm Springs Creek. Silver Bow Creek has received wastes from mining activities in Butte and a series of three settling ponds were built on its lower reach to contain smelting wastes from ore processing at the Washoe copper smelter in Anaconda. Until the settling ponds were constructed in 1954-55, mining and smelting operations discharged wastes directly into the creek and these wastes moved into the Clark Fork River unimpeded and untreated. Over the interval from the 1880's until the mid-1950's, many thousands of tons of effluent found their way into the upper Clark Fork River drainage. Since the construction of the settling ponds and the subsequent liming treatment of the industrial wastes, contaminant input to the river from the ponds decreased dramatically except for a few occasions when the dikes were breached.

In addition to the mining and smelting wastes transported downstream in the river, river-borne tailings have been deposited across the flood plain in the Deer Lodge Valley, causing significant impacts to riparian systems (for example, 7,8). Remobilization of contaminated flood plain sediments may provide a source of continued contaminant input to the Clark Fork River (6). The extent of the impacts to the river and adjacent riparian areas downstream have not been fully delineated.

In November 1981 the Montana Department of Health and Environmental Sciences discovered elevated arsenic levels in water from four community drinking wells in Milltown, Montana. Arsenic concentrations ranged from 0.22 to 0.51 mg/L in the wells. These levels caused immediate concern on the part of State and local health officials since the Federal Safe Drinking Water Standard for arsenic specifies 0.05 mg/L as the upper safety limit. A reconnaissance hydrogeological study identified four possible sources of the arsenic contamination: (1) a wood products mill north of the wells, (2) an abandoned industrial dump southeast of the wells, (3) the adjacent Milltown Reservoir containing an unknown quantity of smelting and mining sediment from upriver, and (4) a deep bedrock ground water system underlying the contaminated reservoir (12).

Noting previous work on heavy metal concentrations in the accumulated reservoir sediment (1), we thought that the reservoir would be the most probable source of the well contamination and obtained four grab samples of sediment in February 1982 by cutting through the ice. These sediment samples contained from 54 to 135 µg/g arsenic, 5 to 95 µg/g lead, 259 to 1357 µg/g manganese, and 66 to 2880 µg/g zinc. As a result of the hydrologic work and the sediment metal levels, the Environmental Protection Agency (EPA) ranked the Milltown Reservoir as site 198 of the initial 400 Superfund sites. In July 1983 we began a study of Milltown Reservoir sediments as part of a Remedial Investigation funded by EPA and the Montana State Solid and Hazardous Waste Bureau to evaluate the sediments as the likely source of arsenic contamination of the ground water in Milltown. We found arsenic, copper, zinc, and other heavy metal concentrations to be highly and significantly elevated in the Clark Fork arm of the Milltown Reservoir as compared to both the Blackfoot arm of the reservoir and levels reported in the literature (5,6,13).

Milltown Reservoir is the first major impoundment below the smelting and mining districts in the Anaconda-Butte area and may have trapped most of the sediment-carried metals. However, occasional releases from the Warm Springs settling ponds have occurred and eyewitness reports tell of the Clark Fork River "running red" with sediment (R.C. Averette, USGS Water Resources Division). If the "red" sediment contained large amounts of heavy metals and arsenic, some portion may have continued to repositories downstream from Milltown Reservoir. Addition of sediment from other large tributaries (Bitterroot, Flathead, Jocko, and Thompson Rivers) below Milltown may have diluted the metals passing through Milltown so that the reservoirs downstream may be relatively uncontaminated. To explore for the lower boundary of mining and smelting impacts to the Clark Fork River, we sampled bottom sediments from three downstream impoundments--Thompson Falls, Noxon, and Cabinet Gorge Reservoirs--to see whether the sediments contained elevated heavy metal and arsenic levels.

The objectives of this paper are threefold: (1) to summarize findings at Milltown Reservoir for comparative purposes; (2) to present early findings from sediment extracts from the three downstream reservoirs; and (3) to examine some preliminary downriver trends in arsenic, copper, and zinc concentrations in the reservoir bottom sediments.

## PHYSICAL SETTING

Milltown Reservoir, the first major impoundment on the Clark Fork River, lies approximately 115 river miles downstream from the Warm Springs Ponds (fig. 1). The reservoir is formed by a small dam built in 1907-08 at the confluence of the Clark Fork and Blackfoot Rivers and is currently owned by the Montana Power Company. The dam presently contains five turbines which produce from 2.5 kW at low flow to a maximum of 3.4 kW at high flow (Phil Smith, 1985, Montana Power Company, Missoula). The Milltown Reservoir itself is small, only about 1.23 miles in total length. The reservoir is full of sediment and is therefore quite shallow throughout except for the two main channels of the Clark Fork and Blackfoot Rivers. Due to the large quantities of sediment

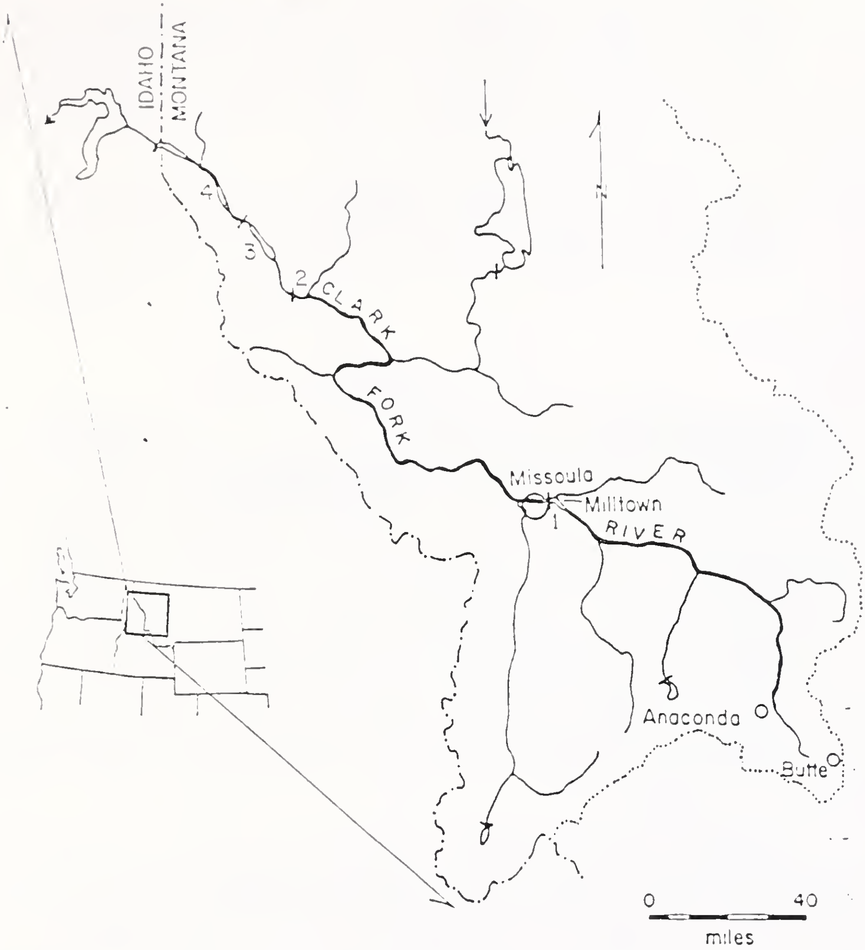

Figure 1. Location map. 1, Milltown Reservoir; 2, Thompson Falls Reservoir; 3, Noxon Rapids Reservoir; 4, Cabinet Gorge Reservoir.

already accumulated, the reservoir probably no longer stores much new sediment and most of the recent suspended sediment load of the Clark Fork probably passes through the reservoir and on downstream.

The second major impoundment on the river is the Thompson Falls Dam, also owned and operated by Montana Power Company. It lies approximately 260 river miles downstream from the Warm Springs Ponds. The reservoir formed by the dam is also relatively small, approximately 2 miles in effective length. The deep Clark Fork channel bisects the reservoir into shallower southern and northern portions. Most of the sediments are sandy; small areas of medium to fine silt deposition occur along the banks.

Noxon Rapids Dam lies roughly 320 river miles downstream from the Warm Springs Ponds. Built in 1959, it has a maximum generating capacity of 554,000 kW and is owned and operated by Washington Water Power Company (WWPC). The reservoir behind the dam covers 8,000 surface acres and can exceed 150 feet in depth. Sediments in the mainstem of the reservoir are predominantly medium and fine silts with little sand and very little clay. Broader areas of the reservoir are accumulating more sediment than the narrow portions.

The final hydroelectric impoundment above Lake Pend Oreille is the Cabinet Gorge Dam which lies 25 miles downriver from Noxon Rapids Dam and approximately 345 river miles downstream from the Warm Springs Ponds. Also owned and operated by WWPC, the facility was constructed in 1952 and has a generating capacity of 230,000 kW. In the lower 15 or 16 miles of the reservoir, sediment is accumulating in only the broad areas of the reservoir.

## METHODS

### Sample Collection

Grab samples of bottom sediment were taken in each reservoir to assess the presence or absence and lateral distribution of arsenic and other metals. Each grab sample was collected with a Peterson dredge. The sediment that had contacted the interior metal surface of the dredge was discarded; the remaining sediment was scooped into a previously acid-washed plastic quart container. The full container was capped and stored in ice for transport to the laboratory. At Milltown Reservoir 27 grab samples were collected in the Clark Fork arm of the reservoir; 10 grabs were collected from the Blackfoot arm of the reservoir (fig. 2). At Thompson Falls Reservoir seven grab samples were collected (fig. 3). Fourteen grab samples were collected from Noxon Reservoir due to its larger size and the *a priori* judgment that most fine sediments would accumulate there (fig. 4). These grab sample sites included two sites for local background: the upper mouths of Vermilion Creek and Trout Creek. Seven grab samples were taken from Cabinet Gorge Reservoir between the town of Noxon on the upstream end and the Rock Islands toward the downstream end of the reservoir (fig. 5). One sample was taken within the mouth of the Bull River as a local background reference.

Due to the shallow depth of the Milltown Reservoir, core samples were taken there with a hand-emplaced coring tube of PVC. The inner core tube liner consisted of acid-washed, fitted 10-cm long sections of PVC tube. When the corer was removed, the individual inner core tube sections were removed and capped, then stored in ice for transport to the lab (for details see 13). The lower reservoirs, being considerably deeper, necessitated using a gravity corer. The corer was lined with a clear acetate tube which was acid rinsed then rinsed with reservoir water before each use. This corer could sample up to 45 cm depths. Most cores collected were 25 cm long. Several cores hit gravel at approximately 35-40 cm. Each core was extruded and divided into 5-cm intervals, stored in acid-washed plastic containers, and kept on ice for transport to the lab. Three cores were collected in the Thompson Falls Reservoir in the shallow embayment near the highway (fig. 3). Five cores were collected from Noxon Reservoir (fig. 4).

### Sample Preparation

All sediment samples were prepared in the laboratory using one of two 3-step extraction schemes. Milltown and Blackfoot samples were centrifuged, in the case of the grab samples, to remove interstitial water. Core samples had the interstitial water removed by nitrogen gas displacement followed by filtration through a 0.45-micron millipore filter (see 13). Samples from the lower reservoirs were subjected to longer transit times between collection and preparation, so instead of displacing the interstitial water, an ammonium

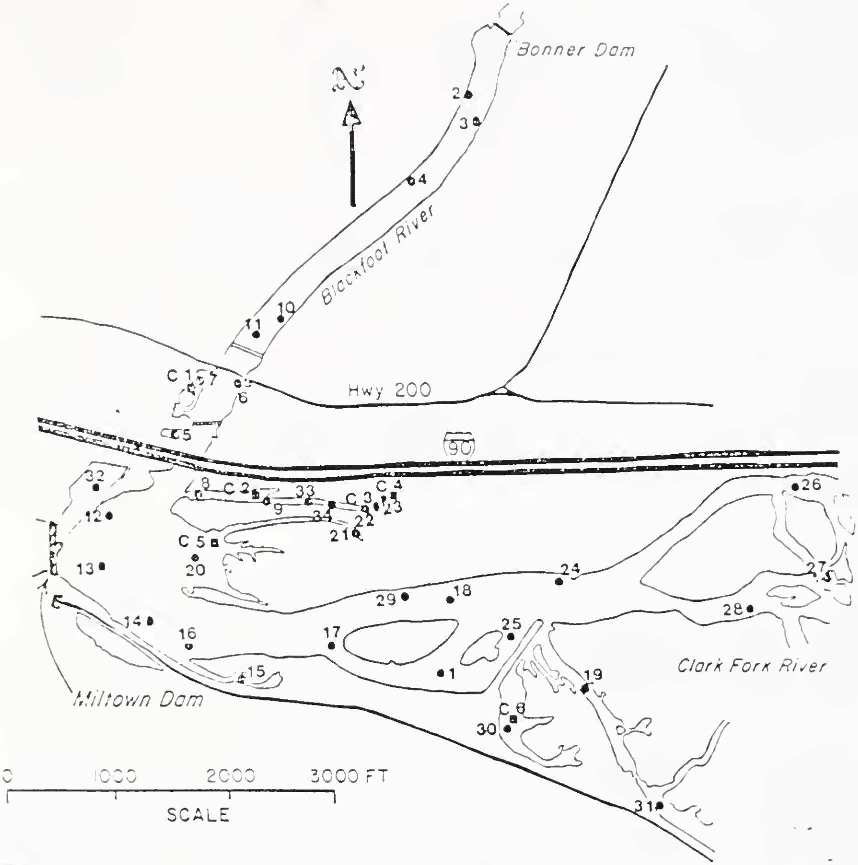

Figure 2. Milltown Reservoir sampling sites. Circles represent grab samples; squares represent cores.

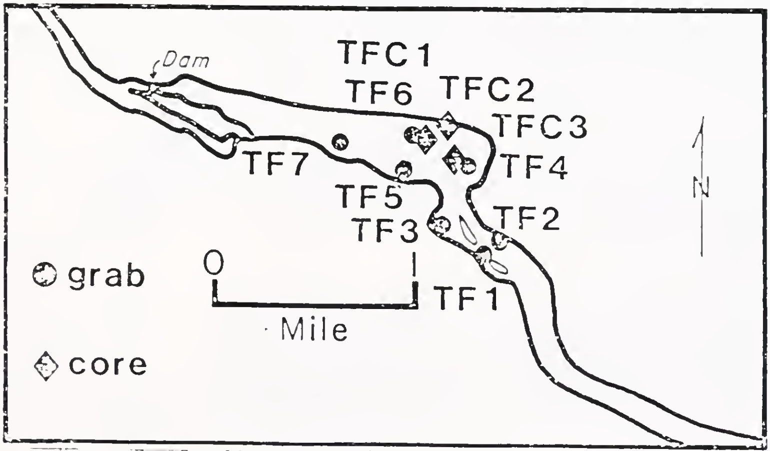

Figure 3. Sampling sites at Thompson Falls Reservoir.

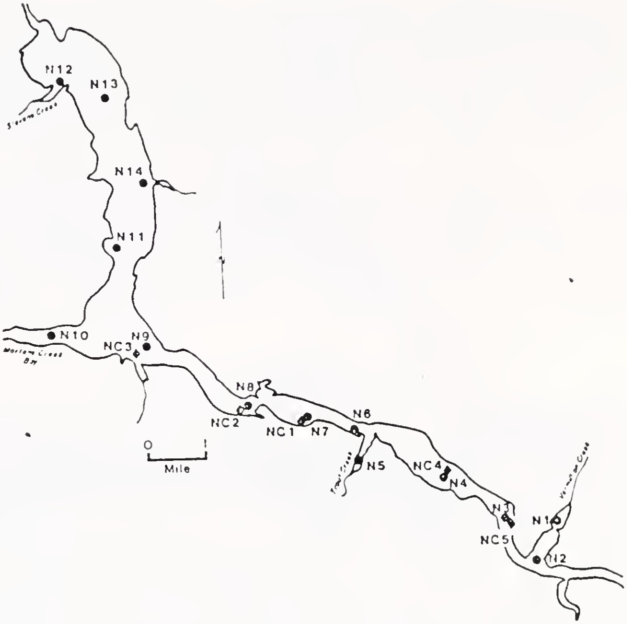

Figure 4. Sampling sites at Noxon Rapids Reservoir. Circles represent grab samples; diamonds represent cores.

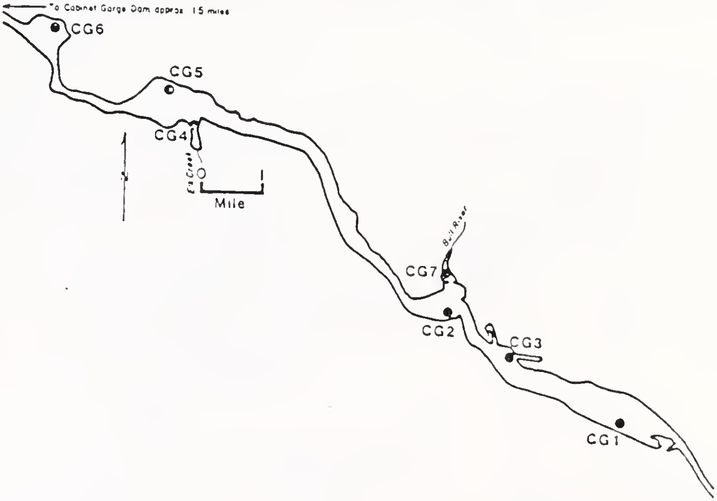

Figure 5. Sampling sites at Cabinet Gorge Reservoir.

acetate (1 M) extraction was used to remove metals held on the ion exchange sites of the sediment (Thompson and others 1983; 4). This extraction was performed by shaking dried, powdered sediment with 1 M ammonium acetate (sediment:solution ratio equaled 1:20) for 2 hours. The mixtures were then centrifuged, the supernatant decanted and filtered through a 0.45-micron millipore filter. The extract was acidified with nitric acid to ph 2 for preservation.

In the second step of both 3-step schemes, residual sediment was dried, repowdered, and extracted with 25% (v/v) acetic acid (3, Thompson and others 1983) to remove metals held in amorphous iron oxides, some manganese hydrous oxides, and some organic fractions. Samples were shaken with 25% acetic acid for 12 hours, centrifuged, and the supernatant filtered through a 0.45-micron millipore filter.

In the final step, "total" metals were determined and represent those metals held in the most resistant fractions, including organic components and silicate lattices. For Milltown Reservoir samples, including the Blackfoot arm samples, arsenic and copper were extracted by 4-hour digestion in hot aqua regia (3:1 HCl: HNO3). Zinc was determined on lithium metaborate fusions of the sediment (2,13). "Total" metal digestions on the lower reservoir sediments are done utilizing hot refluxing nitric acid. These digestions have not been completed and are not discussed here.

## Quality Assurance

Quality assurance activities included (1) reagent blanks analyzed blind for each extract type, (2) replicate extractions or digestions, (3) digestion of NBS sediment standards (SRM 1645 River Sediment and SRM 1646 Estuarine Sediment), (4) splits of sample extracts submitted blind for analysis, (5) duplicate analyses of extracts by the laboratories, and (6) spike recoveries for each element in each matrix.

Metal concentrations in acetic acid blanks were uniformly low. Arsenic averaged 1.7 μg/L in the Milltown study blanks and 0.005 mg/L in the blanks from the lower reservoir study. Copper concentrations in the reagent blanks averaged 0 mg/L and 0.01 mg/L for the Milltown and lower reservoir studies, respectively. Zinc averaged 0 mg/L in the Milltown study blanks and 0.02 mg/L in the lower reservoir study blanks.

For the Milltown study, duplicate acetic acid extracts of the sediments were performed. The average percent differences from the mean of these duplicate extracts were 7.3% for arsenic (n=14), 5% for copper (n=13), and 11.1% for zinc (n=16). Triplicate acetic acid extracts were performed on the lower reservoir sediment samples. The average relative standard deviations were 10.5% for arsenic, 2.4% for copper, and 5.5% for zinc (n=3 for each).

Duplicate analyses of acetic acid extracts performed by the laboratories resulted in average percent differences from the means of 4.9%, 2.1%, and 2.5% for arsenic, copper, and zinc in the Milltown study. The average percent differences from the means of duplicate analyses in the lower reservoir study were 2.1% (n=9), 0.6% (n=9), and 3.3% (n=9) for arsenic, copper, and zinc, respectively.

Spike recovery analyses performed on the acetic acid extracts showed high percent recoveries and low matrix interference effects. For the Milltown study, average percent recoveries for arsenic, copper, and zinc were 97% (n=12), 100% (n=9), and 109% (n=9), respectively. Average percent recoveries for the lower reservoir study samples were 91% (n=9), 105% (n=9), and 97% (n=9) for arsenic, copper, and zinc.

## RESULTS AND DISCUSSION

Table 1 summarizes total and acetic acid extractable concentrations of arsenic, copper, and zinc in the surface grab samples from all reservoirs along the Clark Fork River. Total copper in the Clark Fork arm of Milltown Reservoir ranged from 250 to 1000 µg/g, averaging 449 µg/g. The acetic acid extractable copper, which represents copper held on sites in amorphous iron oxides and some of the manganese hydrous oxides, averaged 241 µg/g and ranged from 100 to 550 µg/g in the Clark Fork portion of Milltown Reservoir. In contrast, total copper in sediments of the Blackfoot arm of Milltown Reservoir averaged only 23 µg/g, with a range of 11 to 32 µg/g. For comparison, table 1 also reports average total copper values for shales and shallow water sediments. Total copper in the Blackfoot arm of Milltown Reservoir is less than the 45 and 56 µg/g reported for shales and shallow water sediments. Total copper in the Clark Fork arm of Milltown Reservoir sediments clearly greatly exceeds these average expected concentrations and concentrations found in the adjacent Blackfoot arm of the reservoir. Acetic acid extractable copper in the Blackfoot arm averaged 5 µg/g with a range of 3 to 8 µg/g. In both arms of Milltown Reservoir the acetic acid fraction of sediment copper constitutes only 25% to 50% of the total copper present.

Table 1.--Average metal concentrations in reservoir sediments along the Clark Fork River (all as µg/g dry weight basis).

| Element | Type | Reservoir<br>Milltown | <br>Blackfoot Arm | <br>Thompson Falls | <br>Noxon | <br>Cabinet Gorge | *Ave. Shale | Shallow Water **Sediment |
|---|---|---|---|---|---|---|---|---|
| Cu | Total | ***449(177) | 23(7) | - | - | - | 45 | 56 |
| | Acetic | 241(121) | 5(2) | 47(12) | 43(6) | 19(7) | - | - |
| Zn | Total | 1770(1430) | 103(23.3) | - | - | - | 95 | 92 |
| | Acetic | 1330(1100) | 11.0(6) | 145(33) | 135(27) | 111(22) | - | - |
| As | Total | 58.6(22.2) | 7.2(1.2) | - | - | - | 13 | 5 |
| | Acetic | 16.0(4.4) | 1.0(0.5) | 2.4(0.5) | 1.9(0.6) | 1.5(0.3) | - | - |

* Values from Turekian and Wedepohl (1961) as cited by Salomons and Forstner (1984)
** Values from Wedepohl (1969, 1978) as cited by Salomons and Forstner (1984)
*** Mean (Standard Deviation)

In the lower three reservoirs for which only acetic acid extract data are presently available, the extractable copper averages 40, 42, and 19 µg/g at Thompson Falls, Noxon, and Cabinet Gorge, respectively. While considerably lower than Milltown Reservoir concentrations, the acetic acid fraction copper in these lower reservoirs exceeds the average Blackfoot arm concentrations by four to eight times. At Thompson Falls Reservoir, acetic acid extract copper concentrations ranged from 32 to 65 µg/g (table 2). In the mainstem of the Noxon Reservoir, acetic acid extractable copper ranged from 31 to 52 µg/g in the surface sediments (table 3). Two sites (N1 and N5), located in the upper mouths of tributary creeks and away from the influence of sediment carried down the mainstem of the reservoir, showed acetic extractable copper concentrations of 4 and 0.3 µg/g. This suggests that local background concentrations for copper in Noxon Reservoir are lower than the Blackfoot arm of Milltown Reservoir upstream. In Cabinet Gorge Reservoir copper concentrations in acetic acid extracts of surface grab samples are lower than at Thompson Falls or Noxon Reservoirs (table 4) and range from 10 to 26 µg/g in the mainstem of the reservoir. As at Noxon, two sites located in the mouths of tributary creeks had very low acetic acid extractable copper concentrations of 2

Table 2.--Metal concentrations in acetic acid extracts of Thompson Falls Reservoir sediments (all reported as µg/g dry weight basis).

| | Mainstem Reservoir Sites | | | | | | |
|---|---|---|---|---|---|---|---|
| Element | TF1 | TF2 | TF3 | TF4 | TF5 | TF6 | TF7 |
| Cu | 32 | -* | 41 | 65 | 45 | 55 | 42 |
| Zn | 125 | 117 | 110 | 213 | 146 | 180 | 126 |
| As | 2.1 | 1.9 | 1.9 | 3.3 | 2.3 | 2.9 | 2.1 |

* missing

Table 3.--Metal concentrations in acetic acid extracts of Noxon Reservoir sediments (all as µg/g dry weight basis).

| | Mainstem of Reservoir Sites | | | | | | | | | | *Intermediate Sites | | **Local Background Sites | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Element | N2 | N3 | N4 | N6 | N7 | N8 | N9 | N11 | N13 | N14 | N10 | N12 | N1 | N5 |
| Cu | 31 | 52 | 49 | 39 | 38 | 46 | 43 | 42 | 39 | 47 | 26 | 22 | 4 | <0.3 |
| Zn | 130 | 201 | 149 | 132 | 120 | 149 | 128 | 123 | 106 | 115 | 88 | 90 | 7 | 10 |
| As | 2.3 | 3.1 | 2.4 | 1.5 | 1.0 | 2.4 | 1.8 | 1.6 | 1.6 | 1.7 | 1.9 | 1.8 | 0.8 | 0.6 |

* Intermediate Sites: N10 at the mouth of Martens Creek
N12 at the mouth of Stevens Creek

** Local Background Sites: N1 in the upper mouth of Vermillion Creek
N5 in the upper mouth of Trout Creek

Table 4.--Metal concentrations in acetic acid extracts of Cabinet Gorge Reservoir sediments (all reported as µg/g dry weight basis).

| | Mainstem Reservoir Sites | | | | | *Local Background Sites | |
|---|---|---|---|---|---|---|---|
| Element | CG1 | CT2 | CG3 | CG5 | CG6 | CG4 | CG7 |
| Cu | 16 | 25 | 10 | 26 | 19 | 2 | <0.3 |
| Zn | 137 | 123 | 80 | 117 | 97 | 21 | 3 |
| As | 1.2 | 1.7 | 1.3 | 1.8 | 1.6 | 0.9 | 0.3 |

* Local Background Sites: CG4 is the mouth of Elk Creek
CG7 is the upper mouth of the Bull River

and 0.3 µg/g, strongly indicating elevated copper levels in the mainstem reservoir sediments compared both to local sediment as well as the Blackfoot upriver.

In the Clark Fork arm of Milltown Reservoir, total zinc concentrations were highly elevated, ranging from 623 µg/g to 5320 µg/g and averaging 1770 µg/g (table 1). These zinc concentrations greatly exceeded both expected zinc concentrations in average shales and shallow water sediment (95 and 92 µg/g, see table 1) and the concentrations found in the Blackfoot arm of Milltown Reservoir. In the Blackfoot arm, zinc levels ranged from 60 to 134 µg/g but averaged 103 µg/g and so approximated expected normal concentrations of zinc. Acetic acid extractable zinc in the Clark Fork portion of Milltown Reservoir formed a large portion of the total zinc present. Zinc concentrations in these extracts ranged from 510 to 3820 µg/g and averaged 1330 µg/g. However, in the Blackfoot arm of the reservoir acetic acid extractable zinc averaged only 11 µg/g, ranging from 2 to 21 µg/g.

Further downriver, acetic acid extractable zinc averaged 145 µg/g (table 1) at Thompson Falls Reservoir, while ranging from 110 to 213 µg/g in the seven mainstem sites. These zinc concentrations are almost 10 times less than those in the Clark Fork arm of Milltown Reservoir but still tenfold greater than acetic acid extractable levels of zinc in the Blackfoot arm of the reservoir. In Noxon Reservoir acetic acid extractable zinc averaged 135 µg/g (table 1) and ranged from 106 to 201 µg/g in the mainstem reservoir grab samples (table 3). The two sites in upper portions of the mouths of Vermilion and Trout Creeks evidenced very much lower acetic acid extractable zinc concentrations--7 and 10 µg/g, respectively. It is not likely that either of these two sites receives much sediment, if any, from the Clark Fork River influenced mainstem of Noxon Reservoir so we consider these zinc levels to represent local sediment input rather than Clark Fork River sediment. Also, the zinc levels at these two sites are comparable to the levels found in the Blackfoot arm of Milltown Reservoir. For both these reasons we are confident that the concentrations of acetic acid extractable zinc at these two sites represent background levels for the area. In Cabinet Gorge Reservoir zinc concentrations in the acetic acid extracts averaged 111 µg/g (table 1), ranging from 80 to 137 µg/g (table 4). In the two sites which represent predominantly local sediment input, zinc concentrations in the acetic extracts were 21 and 3 µg/g. Although levels of zinc in the acetic acid extracts in these lower reservoirs are approximately 10 times lower than the levels in the Clark Fork of the Milltown Reservoir, zinc levels are nevertheless 10 times greater than levels at sites representative of local sediment and levels in the uncontaminated Blackfoot arm of Milltown Reservoir.

Total arsenic concentrations in the Clark Fork arm of Milltown Reservoir averaged 58.6 µg/g (table 1). In the Blackfoot arm, arsenic concentrations averaged 7.2 µg/g. Salomons and Forstner (9) cite 13 and 5 µg/g as representative averages for shales and shallow sediments worldwide, respectively. Acetic acid extractable arsenic averaged 16 µg/g in the Clark Fork arm and only 1 µg/g in the Blackfoot arm of Milltown Reservoir. In the lower three reservoirs, acetic acid extractable arsenic concentrations were low, averaging 2.4, 1.9, and 1.5 at Thompson Falls, Noxon, and Cabinet Gorge. Ranges of arsenic extracted in the acetic acid were also small in these reservoirs (tables 2, 3, and 4). The arsenic levels observed are comparable to those in the Blackfoot arm and to those found at the local background sites in Noxon and Cabinet Gorge Reservoirs. Arsenic does not appear to be significantly elevated in sediments of these lower three reservoirs.

Concentrations of total and acetic acid extractable metals in a single deep core from the Clark Fork arm of Milltown Reservoir are contrasted in figures 6 and 7 for copper and zinc. Total copper in this core varied with depth in the sediment. Concentrations ranged from 1050 µg/g in the surface 3 cm to 10 800 µg/g at 78 cm. Acetic acid extractable copper concentrations ranged from 600 to 1900 µg/g, increasing and decreasing in the same pattern as

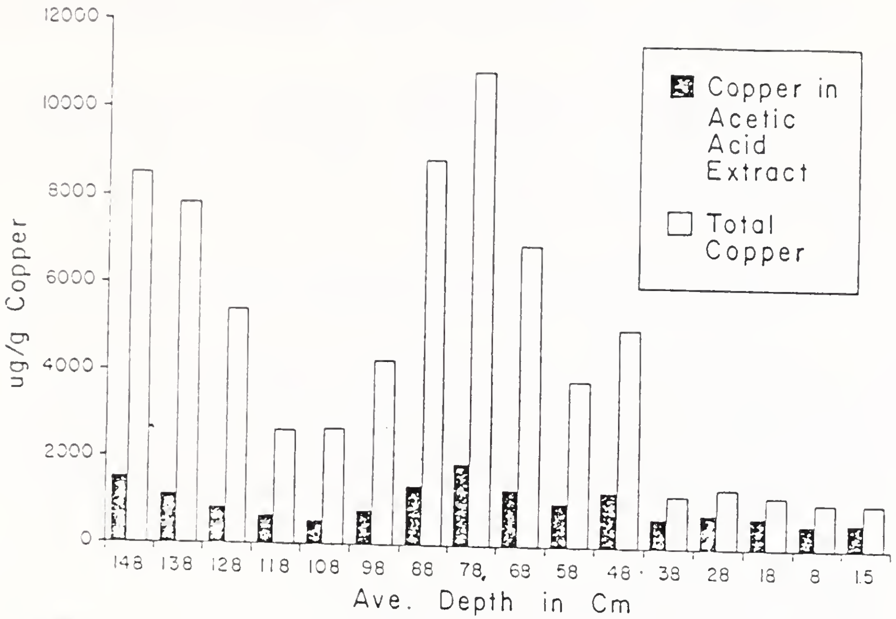

Figure 6. Histogram of copper in core #3 at Milltown Reservoir.

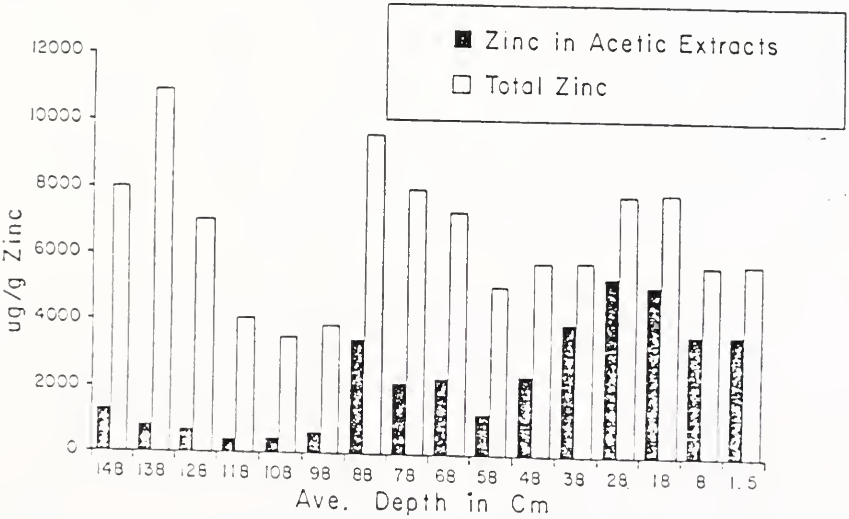

Figure 7. Histogram of zinc in core #3 at Milltown Reservoir.

the total copper levels (fig. 6). As a percentage fraction of the total copper present, the acetic acid extractable copper varied from 60% of the total copper at the lower copper concentrations to less than 20% where total copper was highest.

Total zinc in this core ranged from 3900 µg/g to 10 900 µg/g (fig. 7). Greatest acetic acid extractable zinc concentrations occurred in the surface 40 cm and declined to lowest levels at greatest depth. As a proportion of the total zinc present, 50% to 70% of the zinc could be removed by acetic acid in the upper 40 cm of the core. Less than 15% could be extracted by acetic acid in the lower 50 cm of the core.

Cores taken at Thompson Falls and Noxon Reservoirs were shorter than cores from Milltown Reservoir. In several cores from Noxon Reservoir, the corer tip contained gravel when withdrawn from the reservoir bottom, leading us to conclude that the corer had penetrated to the gravel bed and had sampled the entire sediment profile. Copper, zinc, and arsenic concentrations in acetic acid extracts from a core taken at Thompson Falls Reservoir are presented in table 5. Both copper and zinc concentrations varied with depth in the profile. The concentration of each metal was greatest in the deepest sediment, declined to lowest levels between 15 and 20 cm, then increased again near the surface. Arsenic levels demonstrated a similar pattern, but these differences through the profile were small and may not be significant. The zinc and copper concentrations in this core represent elevated levels of both elements compared to Blackfoot grab and core sample extracts.

Table 5.--Metal concentrations in acetic acid extracts of sediment core #1 from Thompson Falls Reservoir

| | Sediment Depth in Cm | | | | | | |
|---|---|---|---|---|---|---|---|
| Element | 0-5 | 5-10 | 10-15 | 15-20 | 20-25 | 25-30 | Ave. for all Depths (Std. Dev.) |
| Cu | *81 | 54 | 41 | 24 | 45 | 111 | 59(31) |
| Zn | 263 | 145 | 130 | 73 | 134 | 307 | 175(89) |
| As | 3.9 | 3.0 | 3.5 | 1.0 | 2.5 | 2.9 | 2.8(1.0) |

* All concentrations are ug/g dry weight basis

Similarly, copper and zinc in acetic acid extracts from a core in Noxon Reservoir also vary with depth and are elevated with respect to levels of these metals found in acetic acid extracts from the Blackfoot arm of Milltown Reservoir (table 6). This was the deepest core obtained from Noxon Reservoir. Concentrations of all three elements decrease dramatically below 38 cm. The levels of arsenic, copper, and zinc observed in this core between 28 and 41 cm fall within the range found both in the Blackfoot samples and the local background sites for surface sediment in Noxon and Cabinet Gorge Reservoirs. The sediment above 28 cm in depth probably represents fine sediment deposited from the Clark Fork River since construction of Noxon Rapids Dam. Arsenic levels in the acetic acid extracts show the same general pattern as zinc and copper, but again, such low levels are present that arsenic is probably not significantly elevated in these sediments.

Table 6.--Metal concentrations in acetic acid extracts of sediment core #3 from Noxon Reservoir.

| | Sediment Depth in Cm | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Element | 0-3 | 3-8 | 8-13 | 13-18 | 18-23 | 23-28 | 28-33 | 33-38 | 38-41 | Ave. 0-28 |
| Cu | *[illegible]2 | 68 | 44 | 53 | 75 | 69 | 0 | 0 | 0 | 60(12) |
| Zn | 145 | 166 | 136 | 164 | 237 | 236 | 11.9 | 3.9 | 3.9 | 181(44) |
| As | 2.2 | 2.7 | 2.3 | 2.7 | 3.3 | 3.4 | 1.2 | 1.9 | 2.4 | 2.7(0.5) |

* All concentrations are ug/g dry weight basis

Average copper and zinc concentrations for each reservoir, treating the Clark Fork and Blackfoot arms of Milltown Reservoir as separate reservoirs, are plotted in figures 8 and 9. Acetic acid extractable copper and zinc concentrations in the lower three reservoirs show dramatic decreases with distance downriver from the Clark Fork arm of Milltown Reservoir. But, compared to levels in the Blackfoot arm of Milltown Reservoir and to levels at local background sites within Noxon and Cabinet Gorge Reservoirs, copper and zinc concentrations in the acetic acid extractable fraction of the sediment in the three lower Clark Fork reservoirs are elevated. Although copper concentrations are similar at both Thompson Falls and Noxon Reservoirs, zinc levels appear to be slightly lower at Noxon Reservoir. Levels of both metals appear to be lower in sediment of Cabinet Gorge Reservoir. If the acetic acid extractable copper and zinc represent similar portions of the total copper and zinc present in the sediment, as are present in the Clark Fork arm of Milltown Reservoir, total copper and zinc in these lower reservoirs may be twice the levels found in the acetic acid extracts. We expect the total metal concentrations, in combination with the extractable metals reported here, to provide further evidence for influence of mining and smelting activities in the Butte-Anaconda region on metal content of river-transported sediments 280 to 345 miles downriver. To date, we know of no studies of metal content in sediment in the Clark Fork River delta within Lake Pend Oreille. But, based on our findings so far, metal-enriched sediment may have been transported through Cabinet Gorge and into the lake.

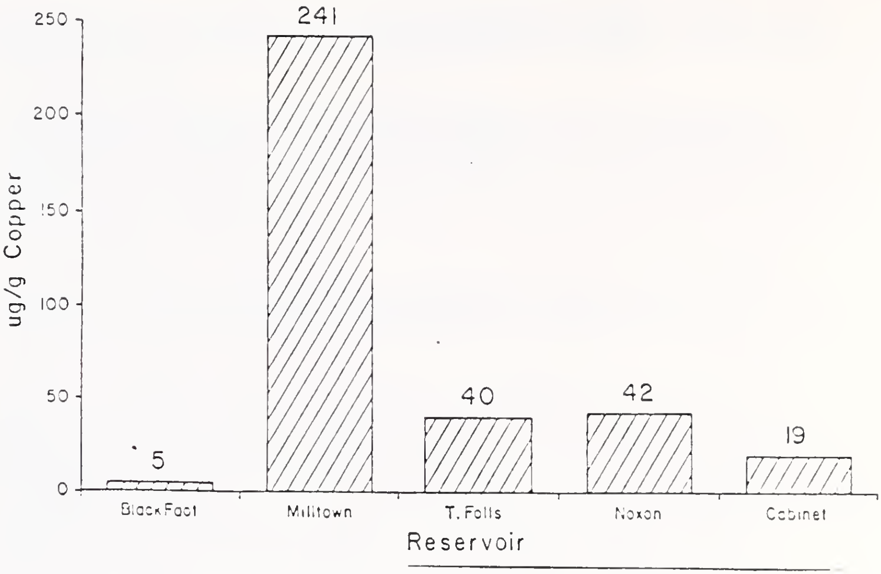

Figure 8. Downriver trends in acetic acid extractable copper.

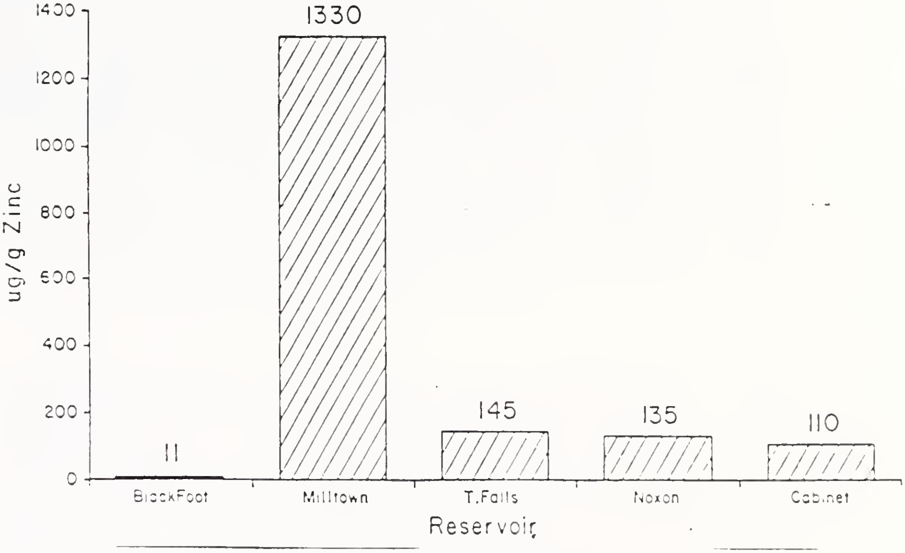

Figure 9. Downriver trends in acetic acid extractable zinc.

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# I. LAKE PEND OREILLE STUDY

# SUMMARY OF DATA COLLECTED DURING 1985 ON LAKE PEND OREILLE, IDAHO BY THE IDAHO DIVISION OF ENVIRONMENT (DEPT. OF HEALTH AND WELFARE)

The following is a summary of the data collected during the 1985 field season by the Idaho Division of Environment in its continuing efforts to assess the limnological conditions in Lake Pend Oreille and the potential for cultural eutrophication of this large lake. This data summary was included at the request of the Montana Water Quality Bureau.

A more complete and definitive report of the results of study efforts conducted to date on Lake Pend Oreille and the lower Clark Fork River is currently in preparation and should be available in early 1986. Those interested should contact the Coeur d'Alene Field Office of the Idaho Division of Environment at (208) 667-3524; 2110 Ironwood Parkway, Coeur d'Alene, ID 83814.

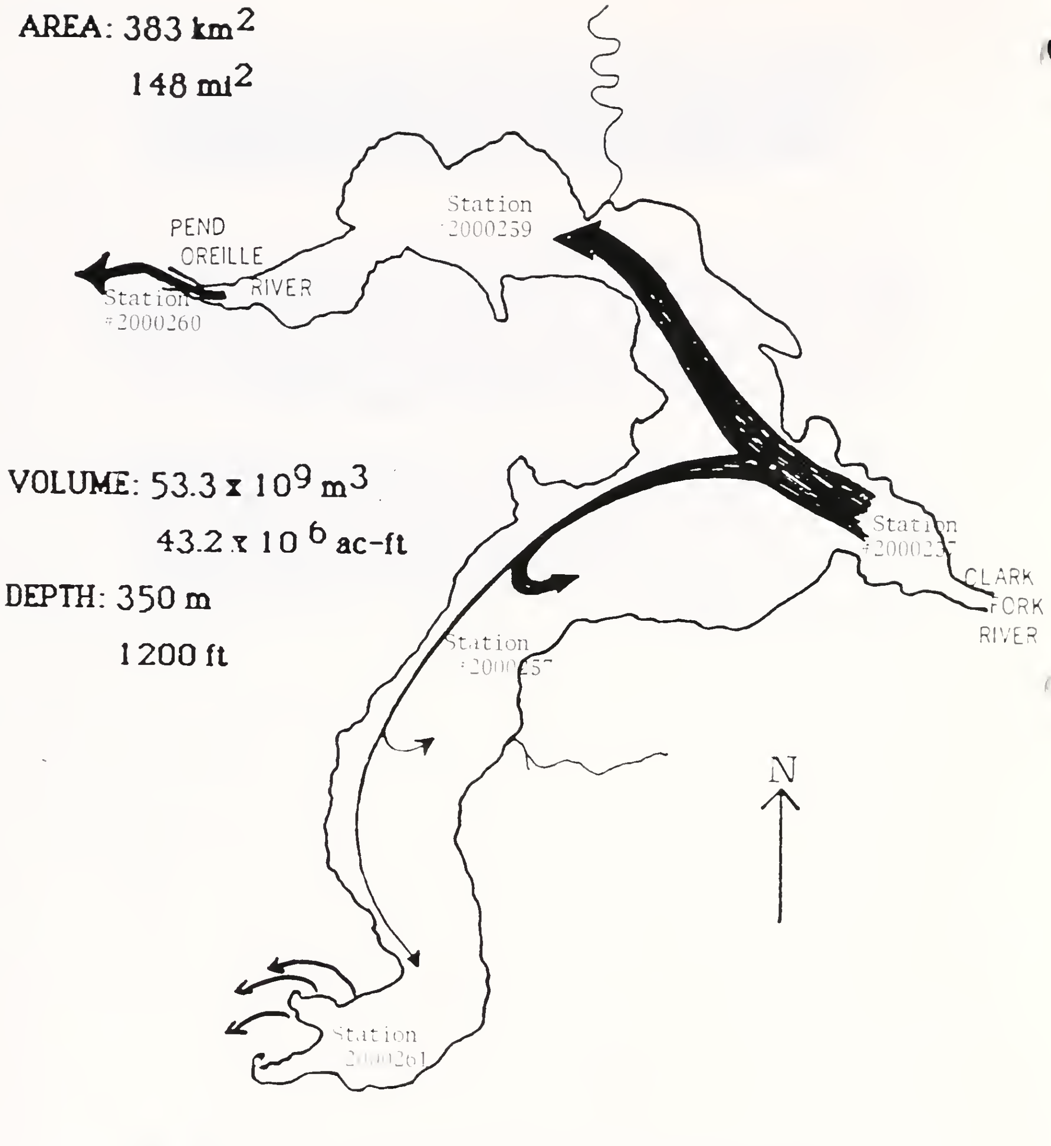


Plate 2. Probable Clark Fork River influence and water exchange patterns in Pend Oreille Lake, Idaho and sampling stations.

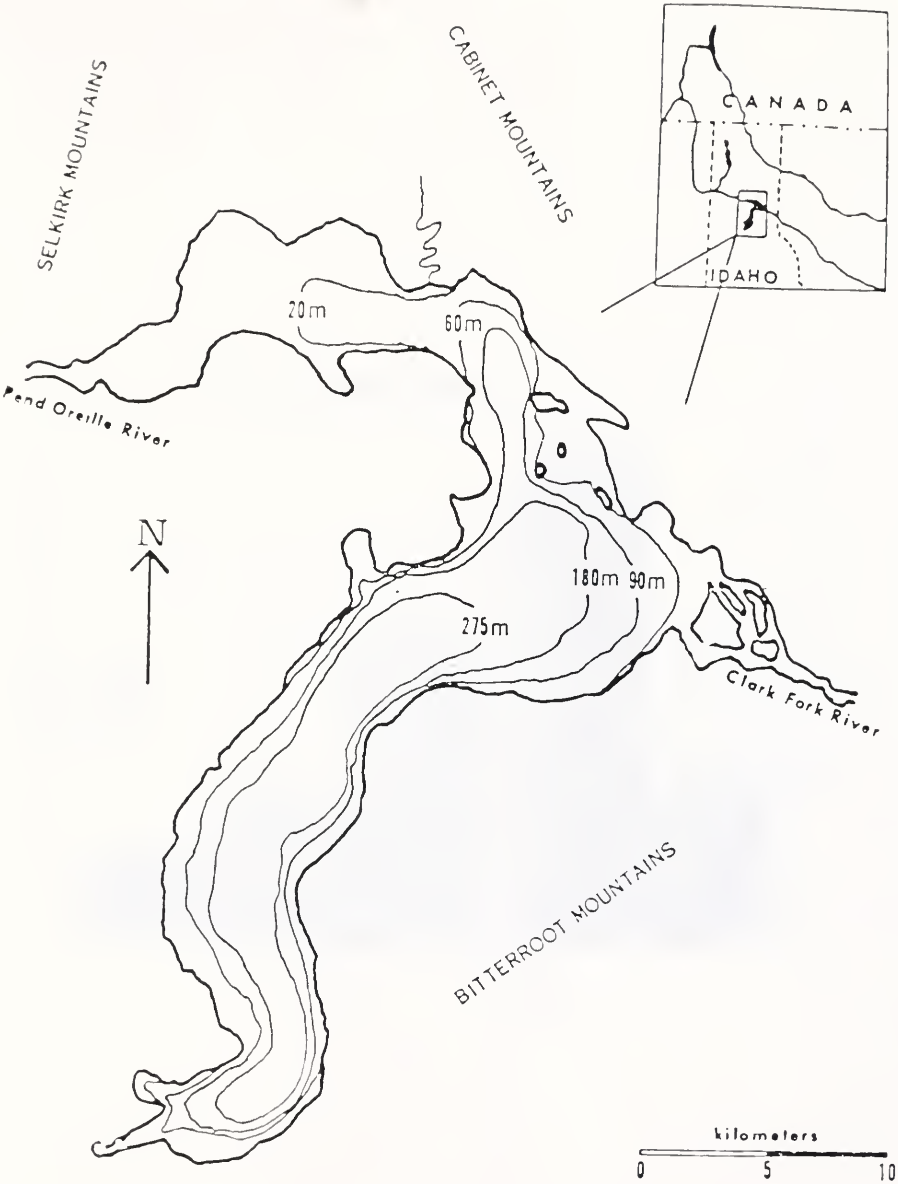


Plate 2. Pend Oreille Lake, Idaho, with depth contours in meters (m)

Figure A. 1985 Average Phosphorus Concentrations

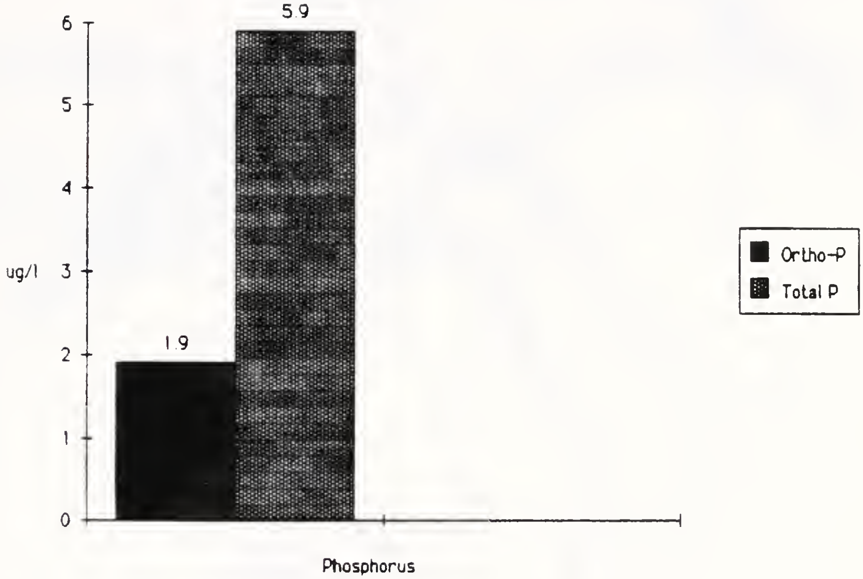


FIGURE 8 1985 Average Nitrogen Concentrations

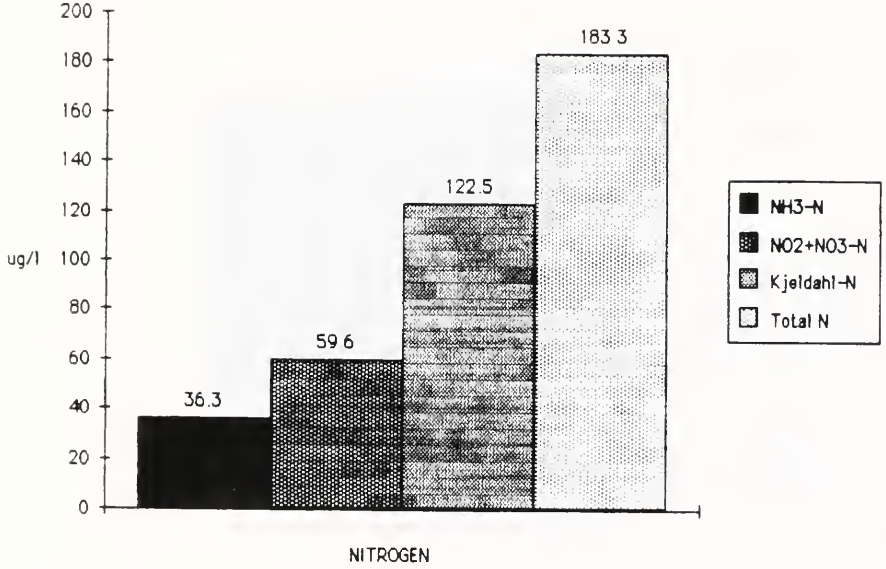


Figure C - Average chlorophyll a concentration.

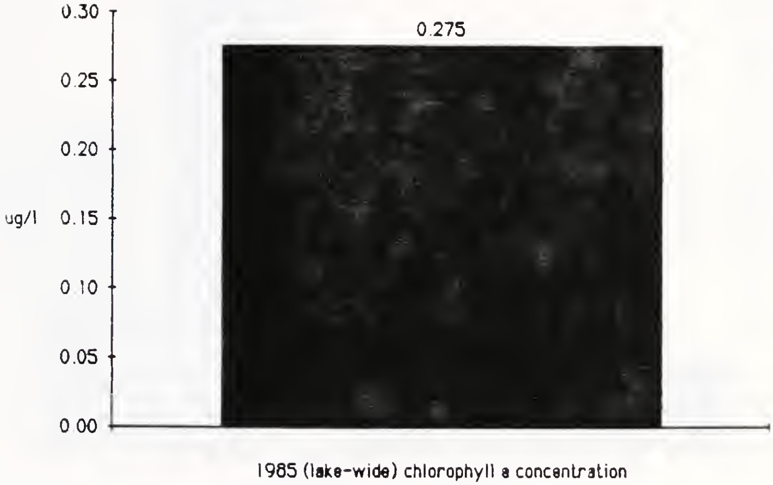


FIGURE D. Summer Mid-Lake (Station 2900257) Temperature Profiles.

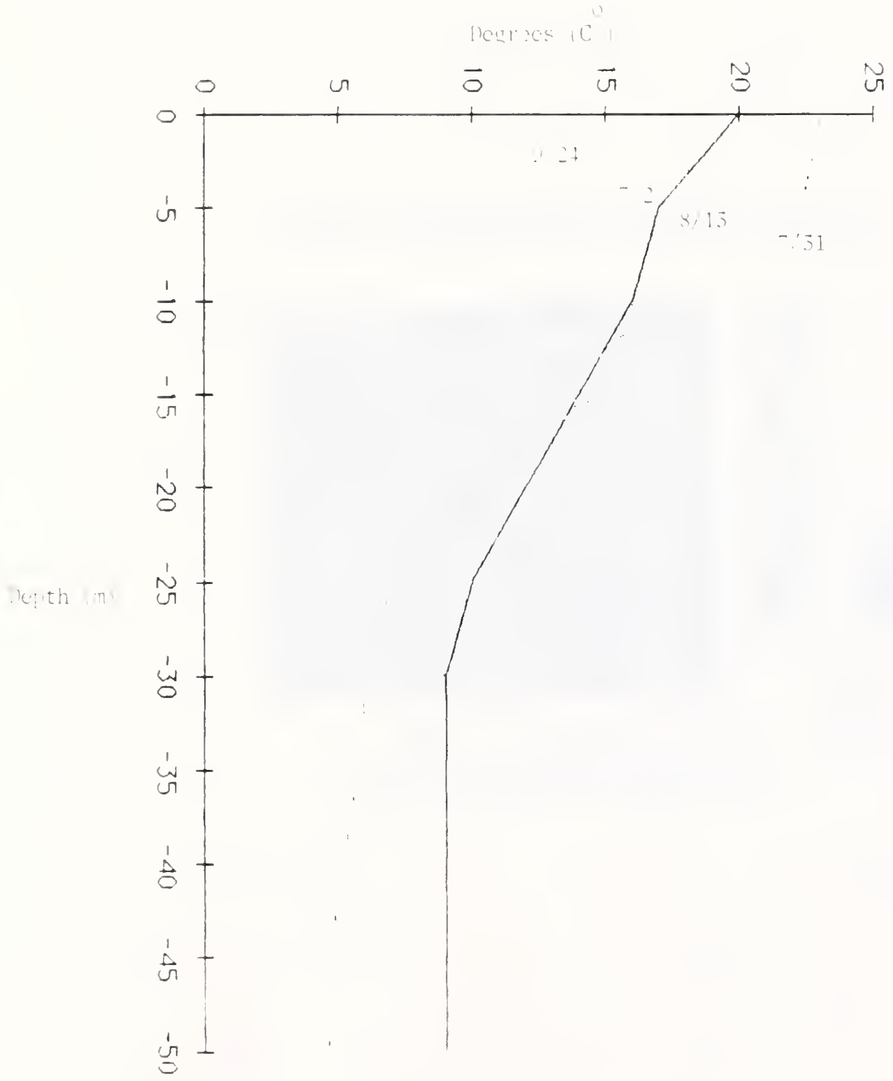
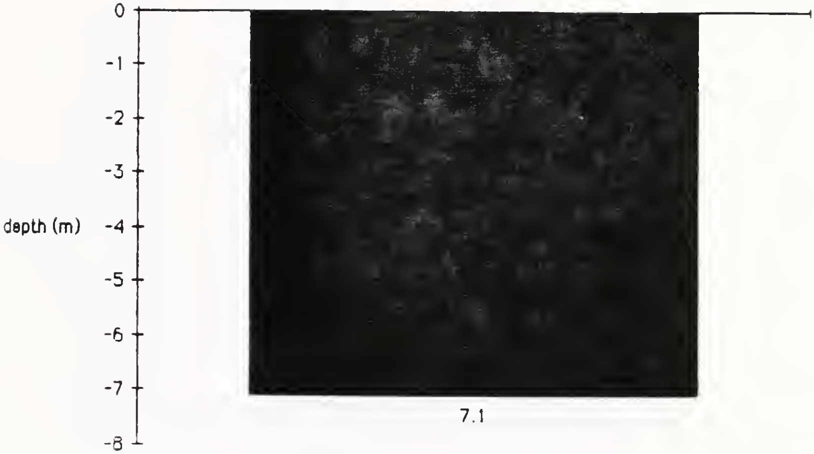
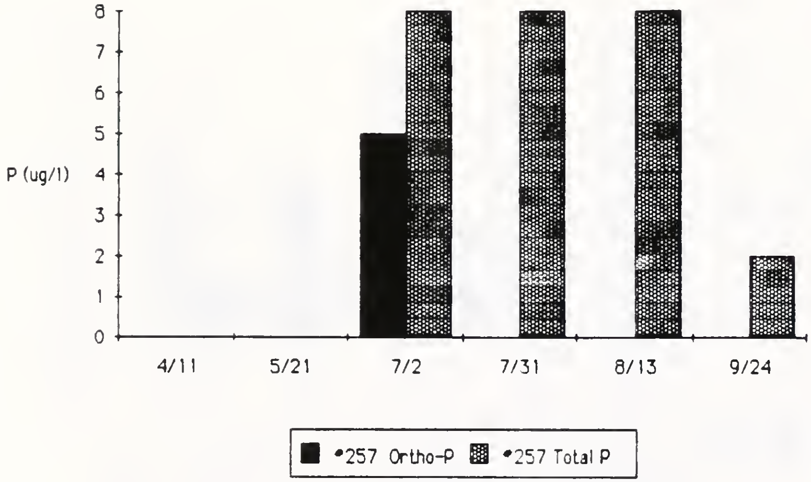


Figure E - 1985 Average Secchi Disk Transparency.



1985 (lake-wide) Secchi Disk Transparency

FIGURE 1. 1985 - STATION #2000257 PHOSPHORUS CONCENTRATIONS



AVERAGES: Ortho-P 0.83; Total P 4.33

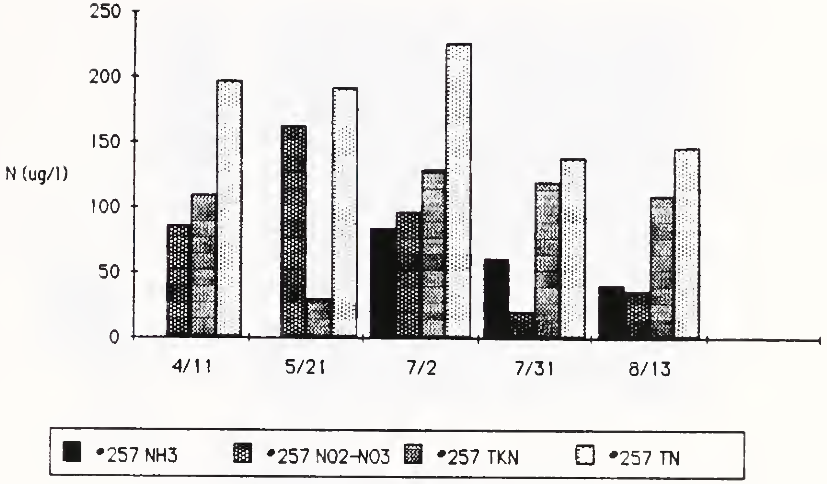
*257 Ortho-P

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 5 |
| 7/31 | 0 |
| 8/13 | 0 |
| 9/24 | 0 |

*257 Total P

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 8 |
| 7/31 | 8 |
| 8/13 | 8 |
| 9/24 | 2 |

FIGURE 2. 1985 - STATION •2000257 NITROGEN CONCENTRATIONS



AVERAGES: NH3 - 37 2; NO2+NO3 - 67 17; TKN - 100 0; TN - 180 6

*257 NH3

| | N(ug/1) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 84 |
| 7/31 | 61 |
| 8/13 | 41 |

*257 NO2-NO3

| | N(ug/1) |
|---|---|
| 4/11 | 87 |
| 5/21 | 162 |
| 7/2 | 97 |
| 7/31 | 20 |
| 8/13 | 37 |

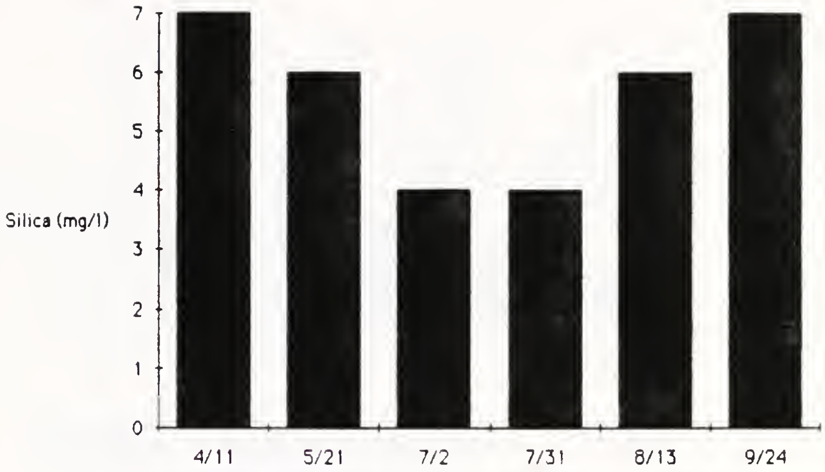
*257 TKN

| | N(ug/1) |
|---|---|
| 4/11 | 110 |
| 5/21 | 30 |
| 7/2 | 130 |
| 7/31 | 120 |
| 8/13 | 110 |

*257 TN

| | N(ug/1) |
|---|---|
| 4/11 | 197 |
| 5/21 | 192 |
| 7/2 | 227 |
| 7/31 | 140 |
| 8/13 | 147 |

FIGURE 3. 1985 - STATION #2000257 SILICA (SIO2) CONCENTRATIONS

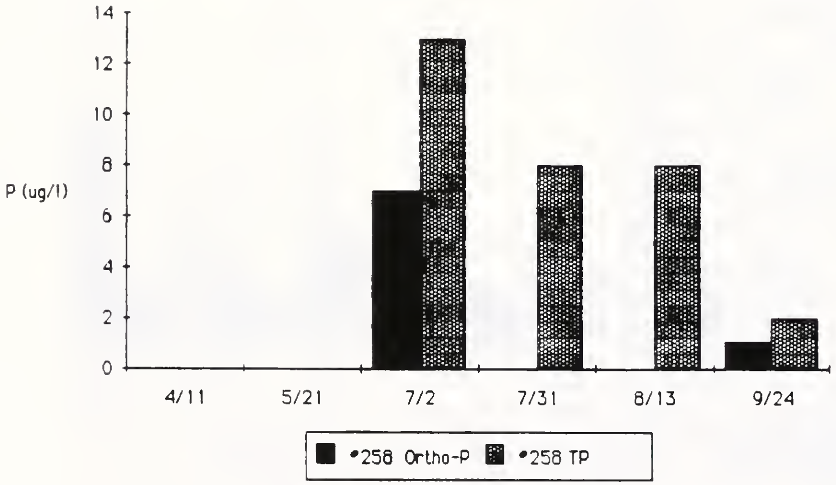


AVERAGE: 5.67 mg/l

*257 SiO2

| | Silica(mg/1) |
|---|---|
| 4 11 | 7 |
| 5 21 | 6 |
| 7 2 | 4 |
| 7 31 | 4 |
| 8 13 | 6 |
| 9 24 | 7 |

FIGURE 4. 1985 - STATION #2000258 PHOSPHORUS CONCENTRATIONS



AVERAGE. Ortho-P 1.33 Total P 5.17

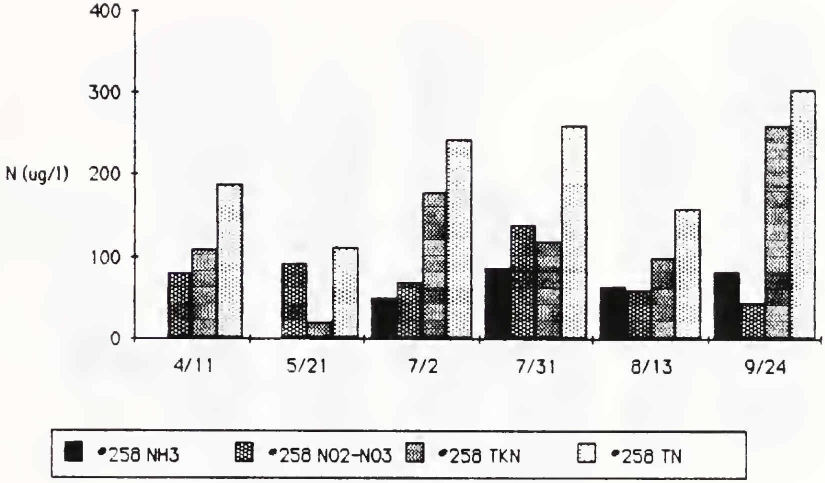
*258 Ortho-P

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 7 |
| 7/31 | 0 |
| 8/13 | 0 |
| 9/24 | 1 |

*258 TP

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 13 |
| 7/31 | 8 |
| 8/13 | 8 |
| 9/24 | 2 |

FIGURE 5. 1985 - STATION •2000258 NITROGEN CONCENTRATIONS



AVERAGES: $NH_3$ - 46.67; $NO_2$+$NO_3$ - 80.17; TKN - 131.67; TN - 211.0

*258 NH3

| | N(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 49 |
| 7/31 | 86 |
| 8/13 | 63 |
| 9/24 | 82 |

*258 NO2-NO3

| | N(ug/l) |
|---|---|
| 4/11 | 79 |
| 5/21 | 91 |
| 7/2 | 68 |
| 7/31 | 140 |
| 8/13 | 58 |
| 9/24 | 45 |

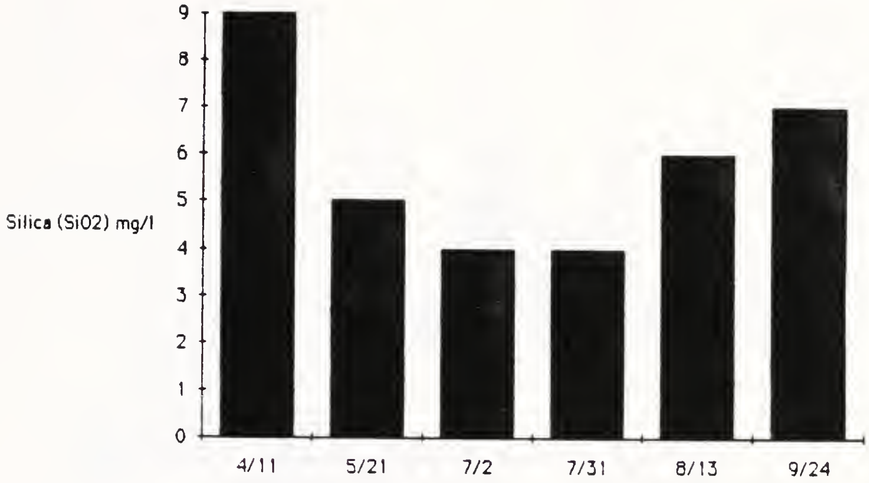
*258 TKN

| | N(ug/l) |
|---|---|
| 4/11 | 110 |
| 5/21 | 20 |
| 7/2 | 180 |
| 7/31 | 120 |
| 8/13 | 100 |
| 9/24 | 260 |

*258 TN

| | N(ug/l) |
|---|---|
| 4/11 | 189 |
| 5/21 | 111 |
| 7/2 | 245 |
| 7/31 | 260 |
| 8/13 | 158 |
| 9/24 | 305 |

FIGURE 6. 1985 - STATION #2000258 SILICA (SiO2) CONCENTRATIONS

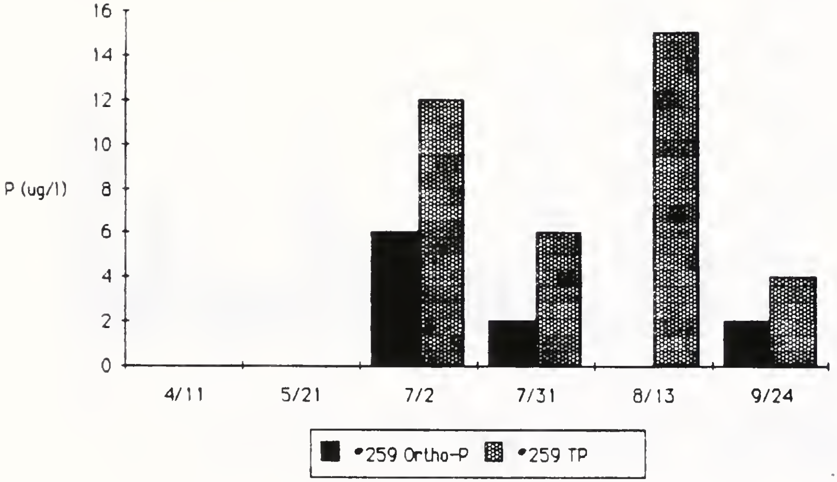


AVERAGE: 5.83 mg/l

*258 SiO2

| | Silica(SiO2)mg |
|---|---|
| 4/11 | 9 |
| 5/21 | 5 |
| 7/2 | 4 |
| 7/31 | 4 |
| 8/13 | 6 |
| 9/24 | 7 |

FIGURE 7 1985 - STATION #2000259 PHOSPHORUS CONCENTRATIONS



AVERAGE. Ortho-P 1 67, Total P 6 17

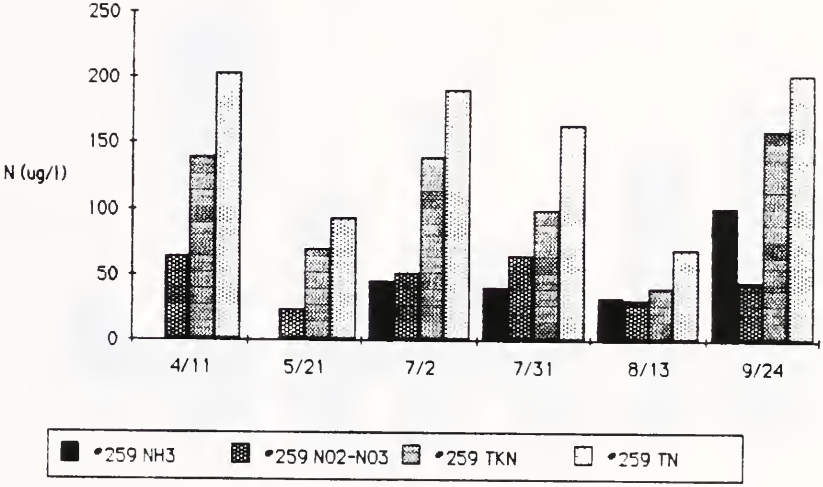
*259 Ortho-P

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 6 |
| 7/31 | 2 |
| 8/13 | 0 |
| 9/24 | 2 |

*259 TP

| | P(ug/l) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 12 |
| 7/31 | 6 |
| 8/13 | 15 |
| 9/24 | 4 |

FIGURE 8. 1985 - STATION #2000259 NITROGEN CONCENTRATIONS



AVERAGES. NH3 - 36.5; NO2+NO3 - 46.17; TKN - 108.33, TN - 154.50

*259 NH3

| | N(ug/1) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 45 |
| 7/31 | 40 |
| 8/13 | 33 |
| 9/24 | 101 |

*259 NO2-NO3

| | N(ug/1) |
|---|---|
| 4/11 | 64 |
| 5/21 | 23 |
| 7/2 | 51 |
| 7/31 | 65 |
| 8/13 | 30 |
| 9/24 | 44 |

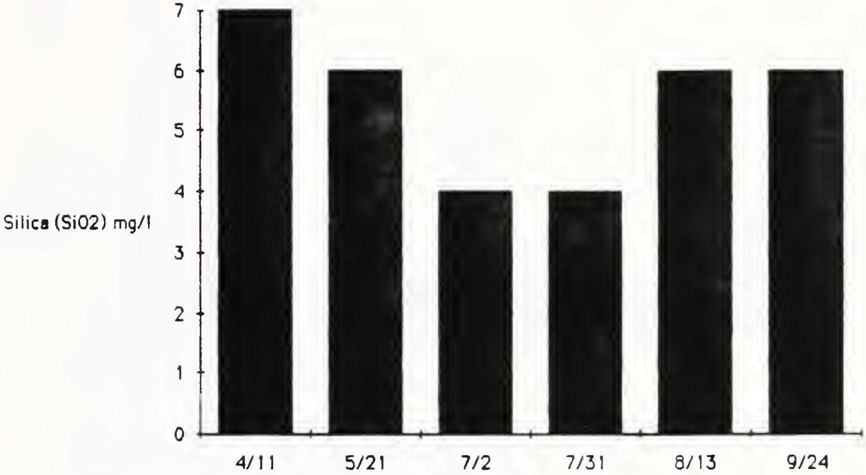
*259 TKN

| | N(ug/1) |
|---|---|
| 4/11 | 140 |
| 5/21 | 70 |
| 7/2 | 140 |
| 7/31 | 100 |
| 8/13 | 40 |
| 9/24 | 160 |

*259 TN

| | N(ug/1) |
|---|---|
| 4/11 | 204 |
| 5/21 | 93 |
| 7/2 | 191 |
| 7/31 | 165 |
| 8/13 | 70 |
| 9/24 | 204 |

FIGURE 9. 1985 - STATION *2000259 SILICA (SiO2) CONCENTRATIONS

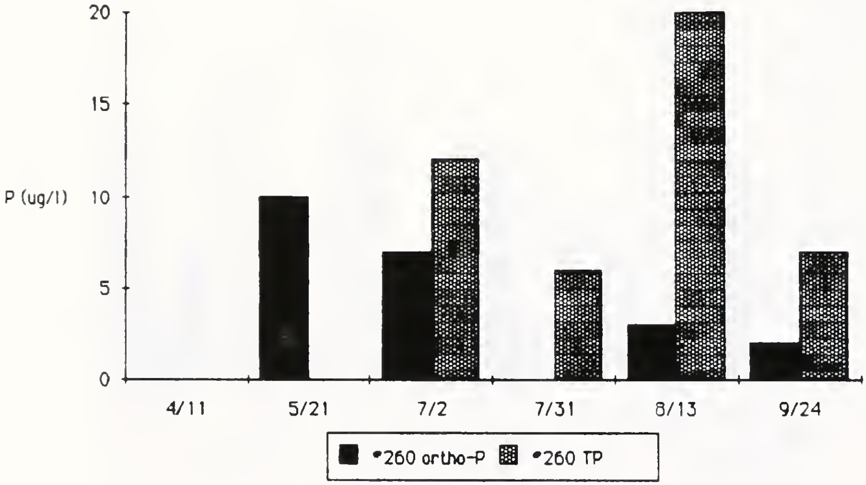


AVERAGE: 5.5 mg/l

*259 SiO2

| | Silica (SiO2)mg |
|---|---|
| 4/11 | 7 |
| 5/21 | 6 |
| 7/2 | 4 |
| 7/31 | 4 |
| 8/13 | 6 |
| 9/24 | 6 |

FIGURE 10. 1985 - STATION *2000260 PHOSPHORUS CONCENTRATIONS



AVERAGE: Ortho-P 3.67; Total P 7.5

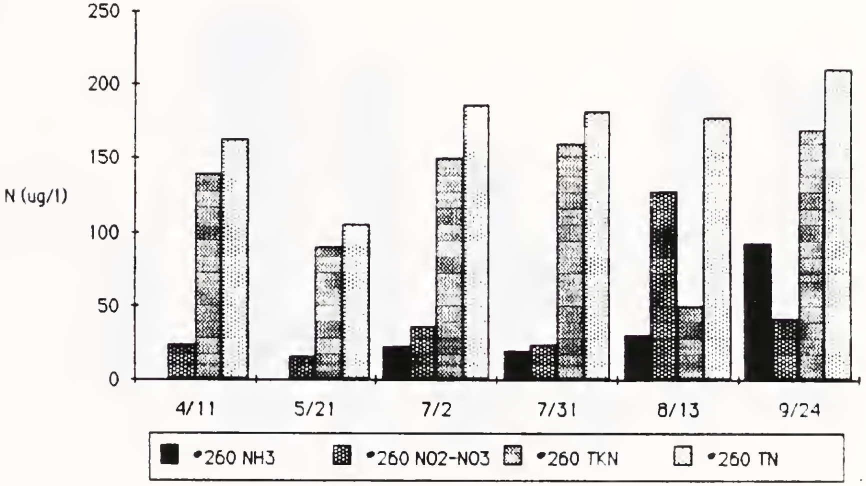
*260 Ortho-P

| | P(ug/1) |
|---|---|
| 4/11 | 0 |
| 5/21 | 10 |
| 7/2 | 7 |
| 7/31 | 0 |
| 8/13 | 3 |
| 9/24 | 2 |

*260 TP

| | P(ug/1) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 12 |
| 7/31 | 6 |
| 8/13 | 20 |
| 9/24 | 7 |

FIGURE 11 1985 - STATION •2000260 NITROGEN CONCENTRATIONS



AVERAGES: NH3 - 27.5; NO2+NO3 - 44.5, TKN - 126.67, TN - 171.17

*260 TKN

| | N(ug/1) |
|---|---|
| 4/11 | 140 |
| 5/21 | 90 |
| 7/2 | 150 |
| 7/31 | 160 |
| 8/13 | 50 |
| 9/24 | 170 |

*260 TN

| | N(ug/1) |
|---|---|
| 4/11 | 163 |
| 5/21 | 105 |
| 7/2 | 186 |
| 7/31 | 183 |
| 8/13 | 178 |
| 9/24 | 212 |

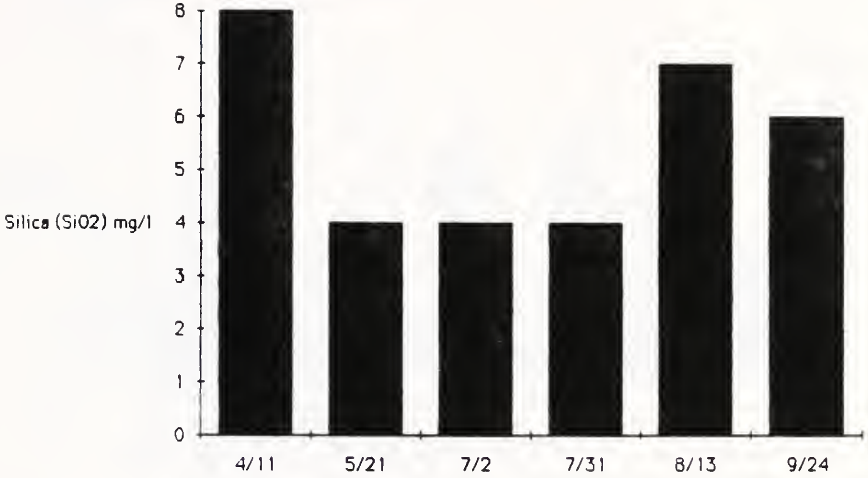
*260 NH3

| | N(ug/1) |
|---|---|
| 4/11 | 0 |
| 5/21 | 0 |
| 7/2 | 22 |
| 7/31 | 20 |
| 8/13 | 31 |
| 9/24 | 42 |

*260 NO2-NO3

| | N(ug/1) |
|---|---|
| 4/11 | 23 |
| 5/21 | 13 |
| 7/2 | 36 |
| 7/31 | 23 |
| 8/13 | 128 |
| 9/24 | 42 |

FIGURE 12. 1985 - STATION *2000260 SILICA (SiO2) CONCENTRATIONS

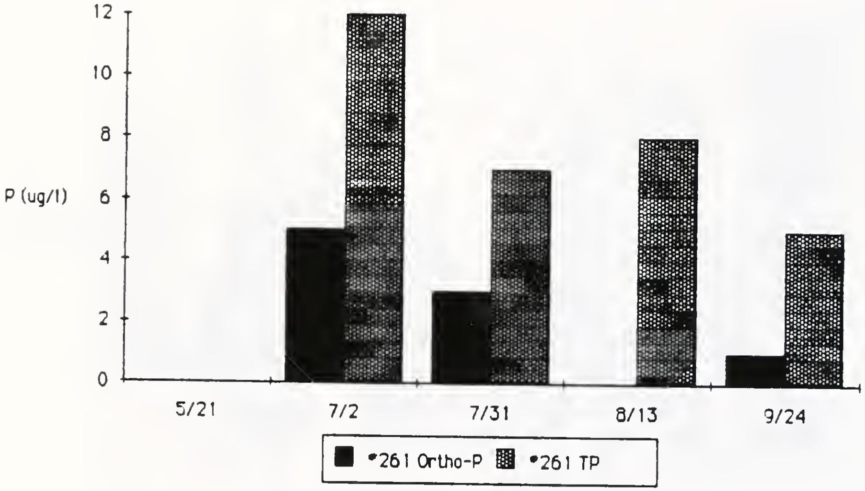


AVERAGE: 5.5 mg/l

*260 SiO2

| | Silica(SiO2)mg |
|---|---|
| 4/11 | 8 |
| 5/21 | 4 |
| 7/2 | 4 |
| 7/31 | 4 |
| 8/13 | 7 |
| 9/24 | 6 |

FIGURE 13. 1985 - STATION *2000261 PHOSPHORUS CONCENTRATIONS



AVERAGES; Ortho-P 1.8, Total P 6.4

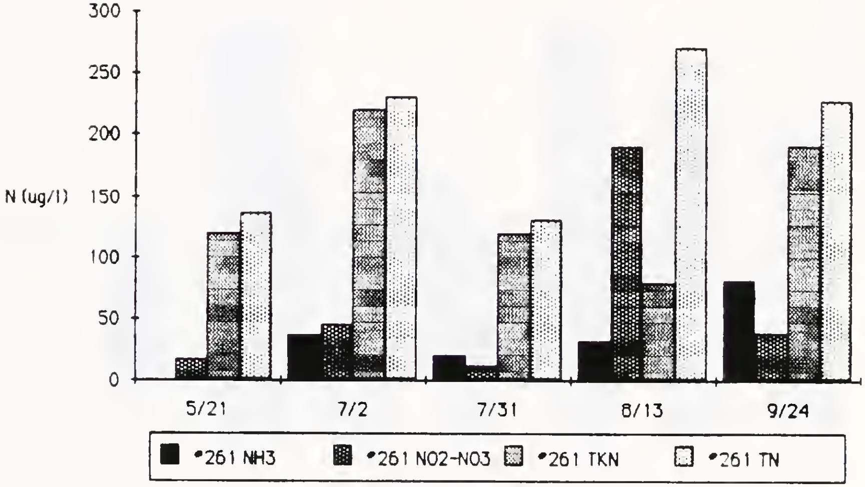
*261 Ortho-P

| | P(ug/l) |
|---|---|
| 5/21 | 0 |
| 7/2 | 5 |
| 7/31 | 3 |
| 8/13 | 0 |
| 9/24 | 1 |

*261 TP

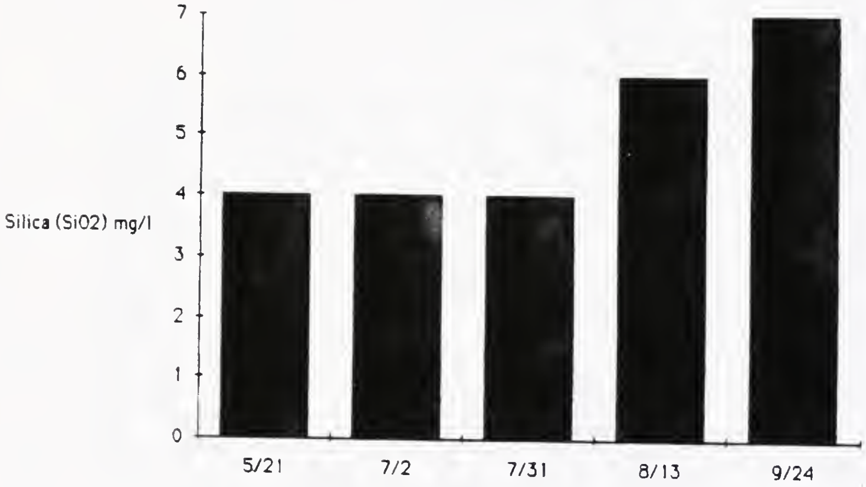
| | P(ug/l) |
|---|---|
| 5/21 | 0 |
| 7/2 | 12 |
| 7/31 | 7 |
| 8/13 | 8 |
| 9/24 | 5 |

FIGURE 14. 1985 - STATION •2000261 NITROGEN CONCENTRATIONS



AVERAGES; NH3 - 33.8; NO2+NO3 - 60.0; TKN - 146.0; TN - 199.2

FIGURE 15. 1985 - STATION *2000261 SILICA (Si02) CONCENTRATIONS

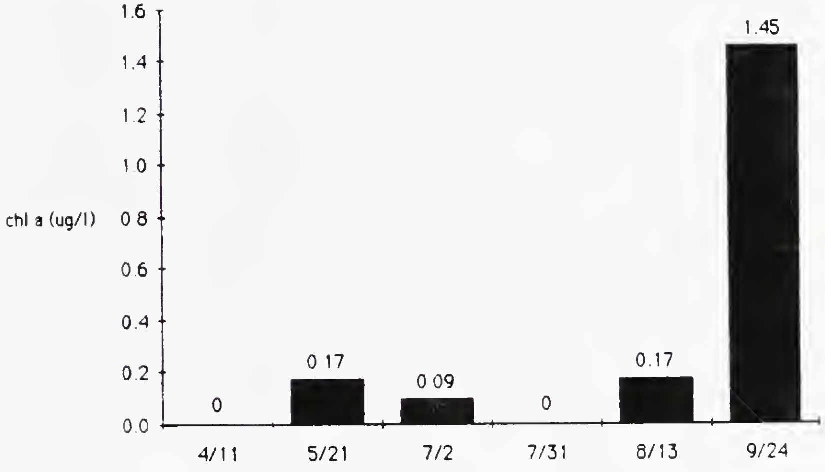


AVERAGE, 5.0 mg/l

*261 - Si02

| | Silica(Si02)mg |
|---|---|
| 5/21 | 4 |
| 7/2 | 4 |
| 7/31 | 4 |
| 8/13 | 6 |
| 9/24 | 7 |

Figure 16 - Station *2000257 chlorophyll a concentration.



Average = 0.313

Figure 17 - Station #2000258 chlorophyll a concentration.

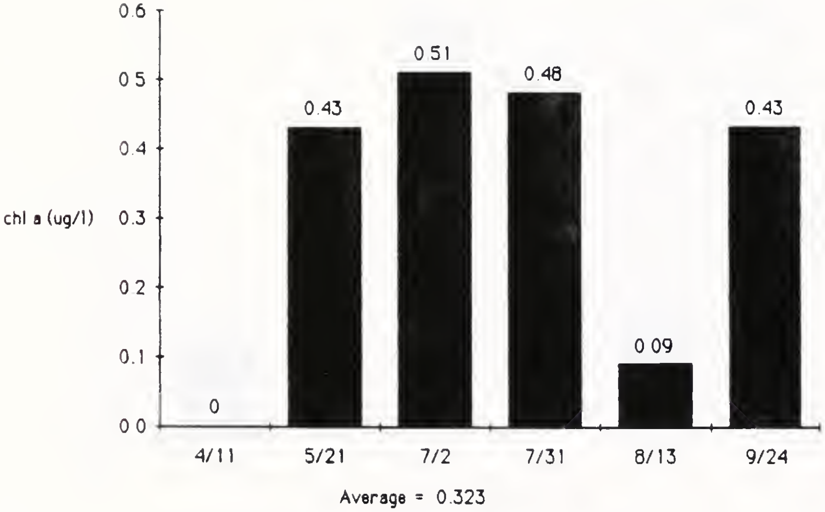
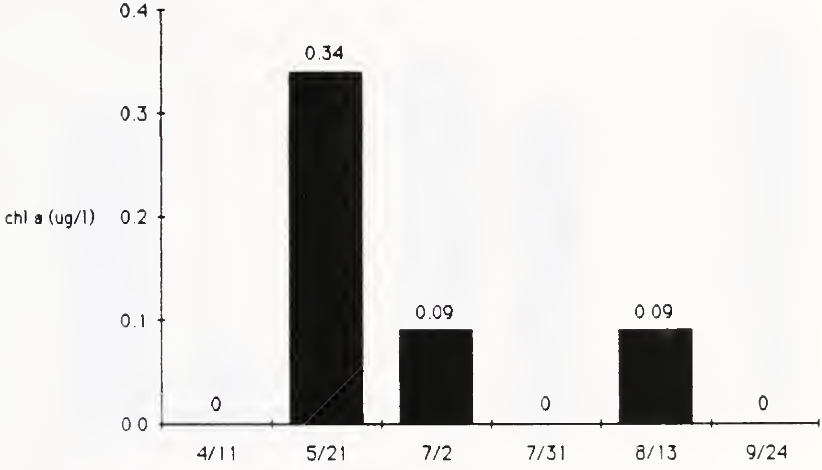
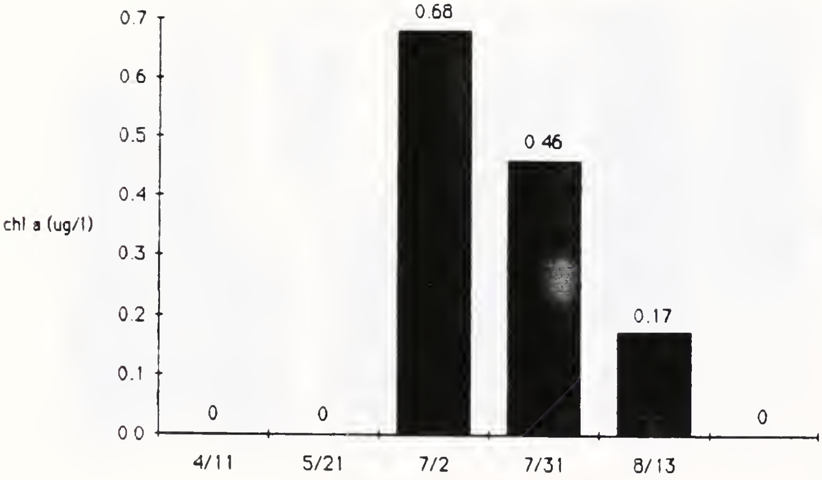


Figure 18 - Station #2000259 chlorophyll a concentration.



Average = 0.087

Figure 19 - Station •2000260 chlorophyll a concentration.



Average = 0.218

Figure 20 - Station *2000261 chlorophyll a concentration.

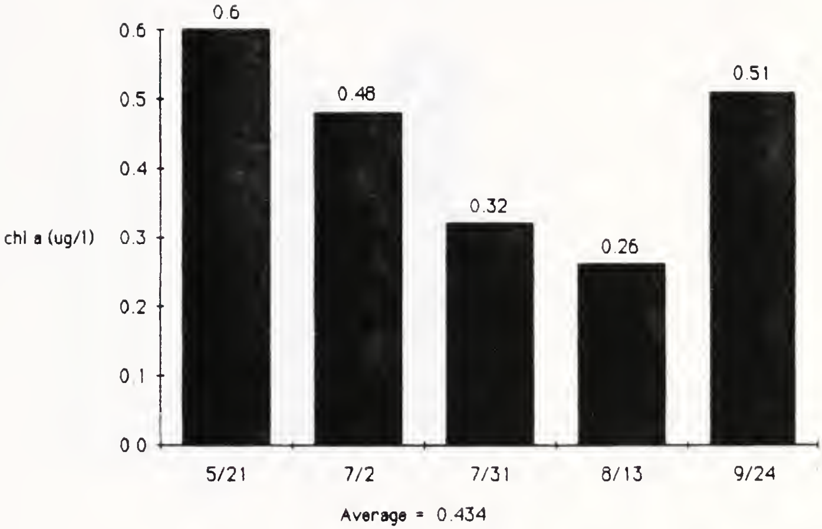
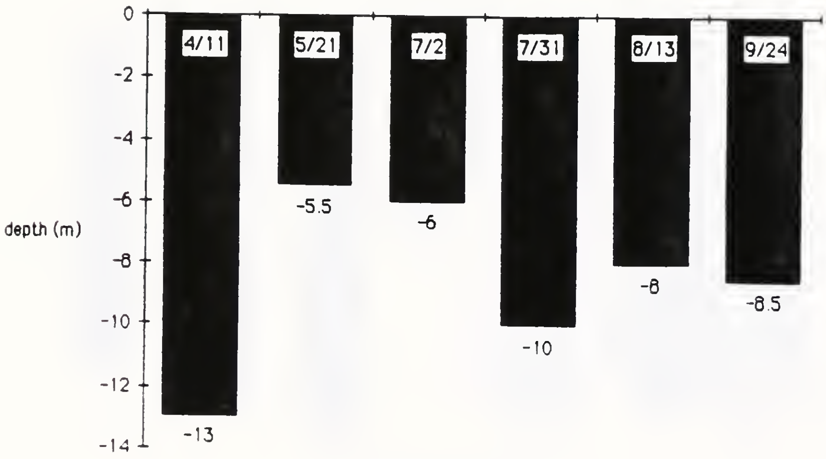
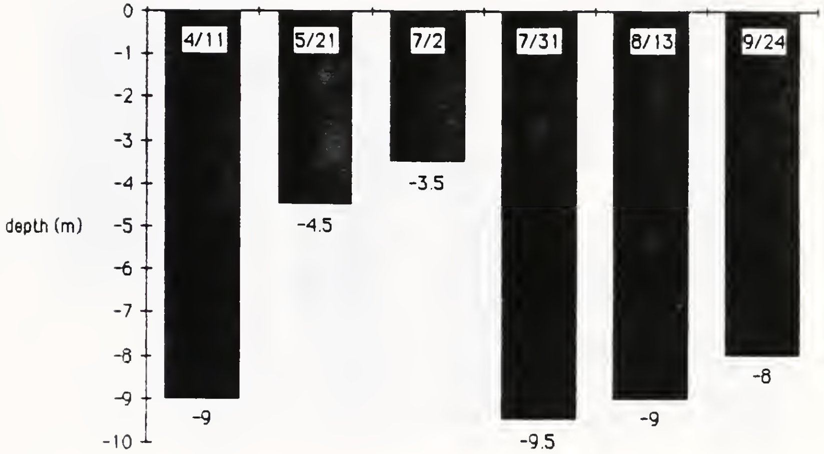


Figure 21 - Station #2000257 Secchi Disk Transparency.



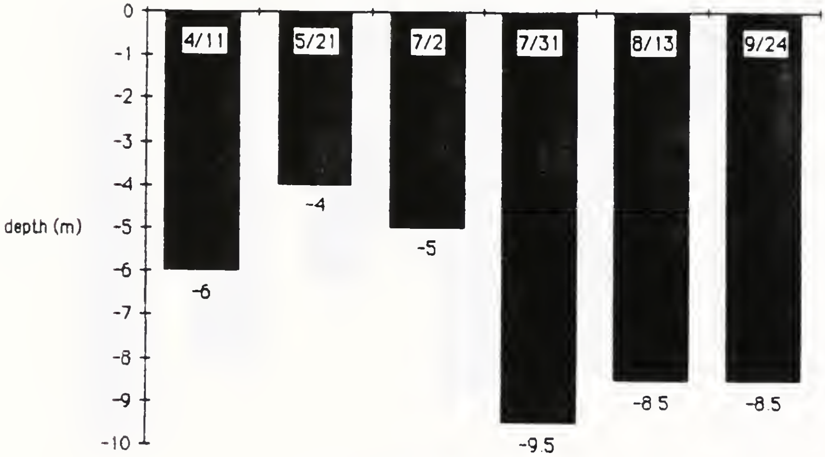
Average = 8.5 m

Figure 22 - Station *2000258 Secchi Disk Transparency.



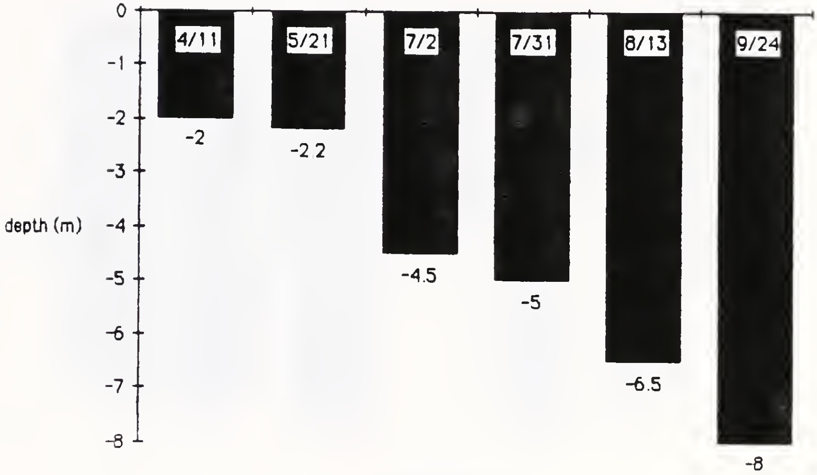
Average = 7.25 m

Figure 23 - Station #2000259 Secchi Disk Transparency.



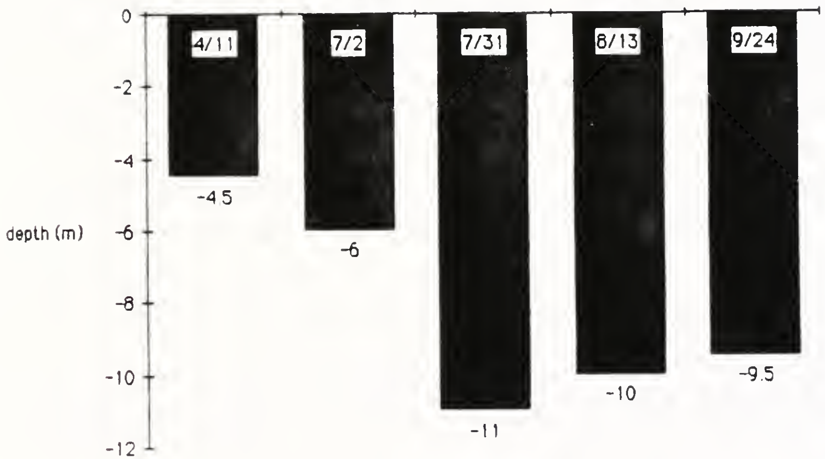
Average = 6.9 m

Figure 24 - Station #2000260 Secchi Disk Transparency.



Average = 4.7 m

Figure 25 - Station #2000261 Secchi Disk Transparency.



Average = 8.2 m

# ACKNOWLEDGMENTS FOR VOLUME I AND II

This intensive water quality study effort would not have been possible without the help of many individuals and agencies.

The EPA provided funding for the water quality study and many of the special studies. The Champion International Corporation funded the fisheries study conducted by the DFWP and a portion of the chronic toxicity bioassays.

Loren Bahls of the WQB designed the original water quality study, prepared the monitoring plan and assisted with field work. WQB staff members Rob Greene, Abe Horpestad, John Jarvie, Mark Kerr, Dick Pedersen and Erich Weber also assisted with field work, including the fatiguing all-night synoptic and diurnal water quality monitoring.

Jarvie also provided the computer listings of the water quality study analysis data.

Kerr sorted the hundreds of benthic macroinvertebrate samples and C. Evan Hornig, now with EPA Region X, provided species identifications and data analysis.

Weber analyzed the periphyton samples and Brenda Harrison of the DHES Chemistry Laboratory Bureau (CLB) performed periphyton and phytoplankton chlorophyll and biomass analyses.

Dennis Braun, Carol Fox, Harrison, John Hawthorne, Kevin Kirley, Rosemary Rowe and Judy Wright of the CLB analyzed the tremendous volume of water and sediment samples collected for the water quality study.

John Standish and staff of Energy Laboratories, Inc. provided the carbon furnace metals analyses of water samples.

DelWayne Nimmo, Loys Parrish, Jim Lazorchek, Denise Link and Maureen Martin of EPA Region VIII, Denver, Colorado and Bruce Binkley of the National Enforcement Investigations Center set up and conducted the rainbow trout and Ceriodaphnia bioassays. Tom Pruitt of the Creston National Fish Hatchery provided larval trout.

Joan Manhart and staff of the EPA Region VIII laboratory provided supporting chemical analyses for the chronic toxicity bioassays and performed the organic analyses of Champion wastewater, river water and foam samples.

Joe Greene and his staff of EPA's Corvallis Environmental Research Laboratory, Corvallis, Oregon conducted the algal bioassay testing and associated chemical analyses.

Rod Berg, George Liknes, Ron Spoon and Dennis Workman designed and conducted the DFWP fisheries study and brown trout bioassays.

Glenn Phillips, Kurt Hill and Workman of the DFWP coordinated the fish flavor and odor evaluations and conducted the crayfish metals study.

David Kicklighter and Jack Stanford performed the University of Montana (UM) riffle community metabolism study.

Carolyn Johns and Johnnie Moore of the UM conducted the reservoir sediment study.

Mike Beckwith, Ed Tulloch and others of the Idaho Department of Environment designed and carried out the Lake Pend Oreille Study.

Charles and Judy Wooley, Tim and Sue Williamson and other members of the Plains Montana Chapter of the Clark Fork River Watchers recorded field observations and measured dissolved oxygen and temperature in the Clark Fork near Plains.

Brace Hayden, Howard Johnson and Ken Knudson of the Montana Governor's Office provided valuable input to study design, monitored study progress and coordinated our activities with those of other individuals.

And lastly, gratitude is expressed to the Clark Fork Technical Advisory Committee and the numerous concerned citizens and citizen's groups such as the Clark Fork Coalition and Clark Fork River Watchers who provided direction to the study and who called our attention to specific problems along the river.

# ERRATUM

Table 5. Results of Organic Analyses of River and Wastewater Foam Samples

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION VIII
ONE DENVER PLACE — 999 18TH STREET — SUITE 1300
DENVER, COLORADO 80202-2413

December 19, 1985

Ref: 8ES-AS

Mr. John Hawthorne
Montana Department of Health and
  Environmental Sciences
Chemistry Laboratory
Cogswell Building
Helena, Montana 59620

Dear Mr. Hawthorne:

Enclosed are final analytical data for Clark Fork, Montana.

Included are:

Semivolatiles analysis for five water/foam samples.

Please call if we can be of further assistance.

Sincerely,

Joan K. Barnes

Joan K. Barnes, Acting Chief
Analytical Support Branch
Environmental Services Division

Enclosures

Table 5. Results of Organic Analyses of River and Wastewater Foam Samples

## ORGANIC LAB RESULTS

## USEPA REGION 8

GREG SAUNDERS - EXTRACTIONS

Date: Dec 12, 1985

Analyst: JOHN [illegible] GC/MS

Case #:

Location: CLARK FORK MONTANA

Date Sampled:

Date Analyzed: 12-3, 4, 5 - 85

Sample Matrix: WATER + FOAM

Parameters: Semi-Volatiles

Sample ID: CLARK FORK 6, 10, 12, 16, 21

Sample Size:

Final Volume:

Extraction Method:

| Sample | Volume Extracted | FINAL VOLUME | DILUTION SCHEME |
|---|---|---|---|
| BLANK | 1 liter | 1 ml | None |
| CLARK FORK #6 | 830 mls | 5 ml | 60 ul → 1 ml |
| CLARK FORK #12 | 850 mls | 1 ml | 100 ul → 1 ml |
| CLARK FORK #21 | 500 mls | 1 ml | 100 ul → 1 ml |
| CLARK FORK #10 | 610 mls | 5 ml | 100 ul → 1 ml |
| CLARK FORK #16 | 870 mls | 1 ml | 100 ul → 1 ml |

Instrument: HP 5993

Detector: MS

Column: DB-5

Temperature:

Flows: ~4 mls/min

Injection Size: 1 ul

Comments: Not enough sample left to analyze a matrix spike. Sample extracts were brown/black in color.

Table 5 Continued

Clark Fork

12-3-85

% Surrogate Recovery

| | 2-FLUORO-PHENOL | D6-PHENOL | D5-NITRO-BENZENE | QUINOXALINE | 2-FLUORO BIPHENYL | D10-PHEN-ANTHRENE | |
|---|---|---|---|---|---|---|---|
| Blank | 39.6 | 37.0 | 53.0 | 60.0 | 61.2 | 91.2 | |

All samples were diluted Surrogate Recoveries for samples were diluted below detection limits.

Table 5 Continued

## Organics Analysis Data Sheet

Laboratory Name: USEPA Region 8
Lab Sample ID: Blank
Tag #:
Sample Matrix: Water

Case Number: Blank for Clark Fork
Site: (Quality Control Blank)
Date Received:
Data Released By:

### Semivolatile Compounds

Concentration: [✓ L], M, H
Date Extracted/Prepared: 11-25-85
Date Analyzed: 12-3-85
Conc Factor: Sample vol = 1 l
Units: ug/liter

MS File: FRC 9598
Percent Moisture:
pH:
Dil Factor: None

| AS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 8-06-2 | 2,4,6-Trichlorophenol | 2u | 87-68-3 | Hexachlorobutadiene | 2u | Alpha BHC | 2u |
| 9-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 5-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 20-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 05-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 8-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 00-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 1-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | u | Endosulfan I | |
| 34-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 19.9 | Dieldrin | |
| 7-86-5 | Pentachlorophenol | | 85-68-7 | Benzyl butyl phthalate | 2u | 4,4'-DDE | |
| 08-95-2 | Phenol | | 84-74-2 | di-n-butyl phthalate | 2.4 | Endrin | |
| 5-85-0 | Benzoic acid | | 117-84-0 | di-n-octyl phthalate | 2u | Endosulfan II | |
| 5-48-7 | 2-Methylphenol | | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 08-39-4 | 4-Methylphenol | | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 5-95-4 | 2,4,5-Trichlorophenol | | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 3-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 2-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 20-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 18-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane Gamma | ↓ |
| 7-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N A |
| 11-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N A |
| 1-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | ↓ | 100-01-6 | 4-Nitroaniline | ↓ | | |

u indicates compound was analyzed for but not detected. Value is the minimum detection limit

Table 5 Continued

Laboratory Name [illegible]

Case No ____________________

**Sample Number**

## Organics Analysis Data Sheet
(Page 4)

Blank for Clark Fork
(QA Blank)

### Tentatively Identified Compounds

12-3 85

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration (ug/l or ug/kg) |
|---|---|---|---|---|
| 1. | Unknown substituted paraffin | | 1166 | |
| 2 | | | | |
| 3 | | | | |
| 4. | | | | |
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Table 5 Continued

## Organics Analysis Data Sheet

Laboratory Name: USEPA Region 8
Lab Sample ID:
Tag #:
Sample Matrix:

Case Number: Craik Fair #6
Site: [illegible] (at Roosevelt Street)
Date Received:
Data Released By: [illegible]

## Semivolatile Compounds

Concentration: [✓ L], M, H
Date Extracted/Prepared: 11-25-85
Date Analyzed: 12-4-85
Conc Factor:
Units:

MS File:
Percent Moisture:
pH:
Dil Factor:
830 mls ⇒ 5ml / 60ml ⇒ 1ml

| CAS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 88-06-2 | 2,4,6-Trichlorophenol | 200.7U | 87-68-3 | Hexachlorobutadiene | 200.7U | Alpha BHC | 200.7U |
| 59-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 95-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 120-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 105-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 88-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 100-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 51-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | | Endosulfan I | |
| 534-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 210.8 | Dieldrin | |
| 87-86-5 | Pentachlorophenol | | 85-68-7 | Benzyl butyl phthalate | 200.7U | 4,4'-DDE | |
| 108-95-2 | Phenol | | 84-74-2 | di-n-butyl phthalate | | Endrin | |
| 65-85-0 | Benzoic acid | | 117-84-0 | di-n-octyl phthalate | | Endosulfan II | |
| 95-48-7 | 2-Methylphenol | | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 108-39-4 | 4-Methylphenol | | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 95-95-4 | 2,4,5-Trichlorophenol | | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 83-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 92-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 120-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 118-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane [illegible] | |
| 67-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N/A |
| 111-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N/A |
| 91-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | | 100-01-6 | 4-Nitroaniline | | | |

U indicates compound was analyzed for but not detected. This is the minimum detection limit

Table 5 Continued

Clark Fork # 6
(at Reserve Street)

Laboratory Name ____________________

Case No ____________________

**Sample Number**

## Organics Analysis Data Sheet
(Page 4)

### Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration (ug/l or ug/kg) |
|---|---|---|---|---|
| 1. | None | | | |
| 2 | | | | |
| 3. | | | | |
| 4. | | | | |
| 5. | | | | |
| 6 | | | | |
| 7. | | | | |
| 8 | | | | |
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| 10. | | | | |
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| 12. | | | | |
| 13. | | | | |
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| 30. | | | | |

Table 5 Continued

## Organics Analysis Data Sheet

| | | | |
|---|---|---|---|
| Laboratory Name: | USEPA Region 8 | Case Number: | Clark Fork #10 |
| Lab Sample ID: | | Site: | [illegible] (Bitterroot River |
| Tag #: | | Date Received: | |
| Sample Matrix: | Water and Foam | Data Released By: | [illegible] |

## Semivolatile Compounds

| | | | |
|---|---|---|---|
| Concentration: | [✓ L], M, H | MS File: | FRK 9604 |
| Date Extracted/Prepared: | 11-25-85 | Percent Moisture: | |
| Date Analyzed: | 12-4-85 | pH: | |
| Conc Factor: | | Dil Factor: | |
| Units: | ug/liter | | 610mls ⇒ 5ml/100ul → 1ml |

| CAS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 88-06-2 | 2,4,6-Trichlorophenol | 163.9u | 87-68-3 | Hexachlorobutadiene | 163.9u | Alpha BHC | 163.9u |
| 59-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 95-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 120-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 105-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 88-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 100-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 51-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | ↓ | Endosulfan I | |
| 534-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 2770.5 | Dieldrin | |
| 87-86-5 | Pentachlorophenol | ↓ | 85-68-7 | Benzyl butyl phthalate | 163.9u | 4,4'-DDE | |
| 108-95-2 | Phenol | 983.6 | 84-74-2 | di-n-butyl phthalate | | Endrin | |
| 65-85-0 | Benzoic acid | 172.1 | 117-84-0 | di-n-octyl phthalate | | Endosulfan II | |
| 95-48-7 | 2-Methylphenol | 163.9u | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 108-39-4 | 4-Methylphenol | 593.4 | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 95-95-4 | 2,4,5-Trichlorophenol | 163.9u | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 83-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 92-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 120-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 118-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane Gamma | ↓ |
| 67-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N/A |
| 111-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N/A |
| 91-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | ↓ | 100-01-6 | 4-Nitroaniline | ↓ | | |

u indicates compound was analyzed for but not detected. Value is the minimum detection limit

Table 5 Continued

Laboratory Name EPA REGION VIII

Case No

**Sample Number**

## Organics Analysis Data Sheet
(Page 4)

Clark Fork #10
(Bitterroot River)

## Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration (ug/l or ug/kg) |
|---|---|---|---|---|
| 1. | TETRADECANOIC ACID |  | 846 | 860.6 |
| 2 | 0.9818 MATCHING FACTOR |  |  |  |
| 3. |  |  |  |  |
| 4. | 1,3,5-Cycloheptatriene |  | 493 | 2180.3 |
| 5 |  |  |  |  |
| 6 | BENZENEPROPANOIC ACID |  | 562 | 1508.2 |
| 7. | 0.9814 MATCHING FACTOR |  |  |  |
| 8 |  |  |  |  |
| 9. | HEXADECANOIC ACID |  | 961 | 2196.7 |
| 10. |  |  |  |  |
| 11 | UNKNOWN SUBSTITUTED PARAFFIN |  | 1161 |  |
| 12. |  |  |  |  |
| 13. |  |  |  |  |
| 14. |  |  |  |  |
| 15. |  |  |  |  |
| 16. |  |  |  |  |
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| 26. |  |  |  |  |
| 27. |  |  |  |  |
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| 30 |  |  |  |  |

Table 5 Continued

## Organics Analysis Data Sheet

Laboratory Name: USEPA Region 8
Lab Sample ID:
Tag #:
Sample Matrix: WATER AND FOAM

Case Number: CLARK FORK # 12
Site: MONTANA (Champion wastewater)
Date Received:
Data Released By: JOHN W. [illegible]

### Semivolatile Compounds

Concentration: [✓ L], M, H
Date Extracted/Prepared: 11-25-85
Date Analyzed: 12-4-85
Conc Factor:
Units: ug/liter

MS File:
Percent Moisture:
pH:
Dil Factor:
850 ml's → 1 ml / 100 ul → 1 ml

| CAS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 88-06-2 | 2,4,6-Trichlorophenol | 23.5U | 87-68-3 | Hexachlorobutadiene | 23.5U | Alpha BHC | 23.5U |
| 59-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 95-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 120-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 105-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 88-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 100-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 51-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | ↓ | Endosulfan I | |
| 534-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 235.3 | Dieldrin | |
| 87-86-5 | Pentachlorophenol | | 85-68-7 | Benzyl butyl phthalate | 23.5U | 4,4'-DDE | |
| 108-95-2 | Phenol | ↓ | 84-74-2 | di-n-butyl phthalate | 45.9 | Endrin | |
| 65-85-0 | Benzoic acid | 72.9 | 117-84-0 | di-n-octyl phthalate | 23.5U | Endosulfan II | |
| 95-48-7 | 2-Methylphenol | 23.5U | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 108-39-4 | 4-Methylphenol | | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 95-95-4 | 2,4,5-Trichlorophenol | | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 83-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 92-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 120-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 118-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane GAMMA | ↓ |
| 67-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N/A |
| 111-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N/A |
| 91-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | ↓ | 100-01-6 | 4-Nitroaniline | ↓ | | |

U indicates compound was analyzed for but not detected. This is the minimum detection limit

Table 5 Continued

Laboratory Name ____________________

Case No ____________________

| Sample Number |
|---|
| |

## Organics Analysis Data Sheet
(Page 4)

Clark Fork # 12
(Champion wastewater)

### Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration ([✓ ug/l] or ug/kg) |
|---|---|---|---|---|
| 1. | UNKNOWN PHTHALATE | | 1130 | |
| 2. | | | | |
| 3. | UNKNOWN SUBSTITUTED PHENANTHRENE | | 1118 | |
| 4. | | | | |
| 5 | HEXADECANOIC ACID | | 954 | 109.2 |
| 6. | 0.9821 MATCHING FACTOR | | | |
| 7. | | | | |
| 8. | 1-PHENANTHRENECARBOXYLIC ACID, | | 1193 | 140 |
| 9. | 1,2,3,4,4a,9,10,10a-OCTAHYDRO-1,4a- | | | |
| 10. | DIMETHYL-7-(1-METHYLETHYL)-, | | | |
| 11. | [1R-(1.ALPHA.,4a.BETA.,10a. | | | |
| 12. | ALPHA.)] 0.9821 MATCHING FACTOR | | | |
| 13. | | | | |
| 14. | BENZENE, 1-METHYL-3-(1-METHYL | | 283 | 36.7 |
| 15. | ETHYL) 0.9808 MATCHING FACTOR | | | |
| 16. | | | | |
| 17. | CYCLOHEXENE, 3-METHYLENE-6- | | 238 | 20.7 |
| 18. | (1-METHYLETHYL) 0.9808 MATCHING FACTOR | | | |
| 19 | | | | |
| 20. | BENZENE, (2-METHYL-1-PROPENYL) | | 345 | 11.8 |
| 21. | 0.8783 MATCHING FACTOR | | | |
| 22. | | | | |
| 23. | | | | |
| 24. | | | | |
| 25. | | | | |
| 26. | | | | |
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There is a distinct cluster of peaks between scans 920-1280.

Table 5 Continued

## Organics Analysis Data Sheet

Laboratory Name: USEPA Region 8
Lab Sample ID:
Tag #:
Sample Matrix: WATER AND FOAM

Case Number: CLARK FORK #16
Site: MONTANA (at Ninemile)
Date Received:
Data Released By: JOHN H. EARNHART

810 mls ⇒ 1 ml / 100 ul ⇒ 1 ul.

### Semivolatile Compounds

Concentration: [✓ L], M, H
Date Extracted/Prepared: 11-25-85
Date Analyzed: 12-5-85
Conc Factor:
Units: ug/liter

MS File: FRN 9608
Percent Moisture:
pH:
Dil Factor:

| CAS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 88-06-2 | 2,4,6-Trichlorophenol | 22.9U | 87-68-3 | Hexachlorobutadiene | 22.9U | Alpha BHC | 22.9U |
| 59-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 95-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 120-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 105-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 88-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 100-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 51-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | ↓ | Endosulfan I | |
| 534-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 319.5 | Dieldrin | |
| 87-86-5 | Pentachlorophenol | | 85-68-7 | Benzyl butyl phthalate | 22.9U | 4,4'-DDE | |
| 108-95-2 | Phenol | | 84-74-2 | di-n-butyl phthalate | | Endrin | |
| 65-85-0 | Benzoic acid | | 117-84-0 | di-n-octyl phthalate | | Endosulfan II | |
| 95-48-7 | 2-Methylphenol | | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 108-39-4 | 4-Methylphenol | | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 95-95-4 | 2,4,5-Trichlorophenol | | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 83-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 92-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 120-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 118-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane GAMMA | ↓ |
| 67-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N/A |
| 111-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N/A |
| 91-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | ↓ | 100-01-6 | 4-Nitroaniline | ↓ | | |

U indicates compound was analyzed for but not detected. This is the minimum detection limit.

Tabel 5 Continued

**Laboratory Name** EPA REGION VIII

**Case No**

Clark Fork #16
(at Ninemile)

**Sample Number**

## Organics Analysis Data Sheet
(Page 4)

### Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration (ug/l or ug/kg) |
|---|---|---|---|---|
| 1. | CYCLOHEXANAMINE, N-CYCLOHEXYL | | 623 | 69.89 |
| 2. | 0.9812 MATCHING FACTOR | | | |
| 3. | | | | |
| 4. | HEXADECANOIC ACID | | 959 | 31.72 |
| 5 | 0.9823 MATCHING FACTOR | | | |
| 6 | | | | |
| 7. | HEPTADECANE AND OCTADECANE | | | |
| 8 | IDENTIFIED | | | |
| 9. | | | | |
| 10. | UNKNOWN SUBSTITUTED PARRAFIN | | 1161 | |
| 11. | | | | |
| 12. | | | | |
| 13 | | | | |
| 14. | | | | |
| 15. | | | | |
| 16. | | | | |
| 17. | | | | |
| 18 | | | | |
| 19 | | | | |
| 20 | | | | |
| 21. | | | | |
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| 24. | | | | |
| 25. | | | | |
| 26. | | | | |
| 27. | | | | |
| 28 | | | | |
| 29 | | | | |
| 30. | | | | |

Table 5 Continued

## Organics Analysis Data Sheet

Laboratory Name: USEPA Region 8
Lab Sample ID:
Tag #:
Sample Matrix: WATER AND FOAM

Case Number: CLARK FORK # 21
Site: MONTANA (Below St. Regis)
Date Received:
Data Released By: JOHN W. [illegible]

### Semivolatile Compounds

Concentration: [✓ L], M, H
Date Extracted/Prepared: 11-25-85
Date Analyzed: 12-5-85
Conc Factor:
Units: ug/liter

MS File: FRN' 9606
Percent Moisture:
pH:
Dil Factor:

500mls ⇒ 1ml / 100ml ⇒ 1ml.

| CAS # | Compound Name | Amount | CAS # | Compound Name | Amount | Compound Name | Amount |
|---|---|---|---|---|---|---|---|
| 88-06-2 | 2,4,6-Trichlorophenol | 40 u | 87-68-3 | Hexachlorobutadiene | 40u | Alpha BHC | 40u |
| 59-50-7 | p-Chloro-m-Cresol | | 77-47-4 | Hexachlorocyclopentadiene | | Beta BHC | |
| 95-57-8 | 2-Chlorophenol | | 78-59-1 | Isophorone | | Delta BHC | |
| 120-83-2 | 2,4-Dichlorophenol | | 91-20-3 | Naphthalene | | Gamma BHC(Lindane) | |
| 105-67-9 | 2,4-Dimethylphenol | | 98-95-3 | Nitrobenzene | | Heptachlor | |
| 88-75-5 | 2-Nitrophenol | | 62-75-9 | N-nitrosodimethylamine | | Aldrin | |
| 100-02-7 | 4-Nitrophenol | | 86-30-6 | N-nitrosodiphenylamine | | Heptachlor epoxide | |
| 51-28-5 | 2,4-Dinitrophenol | | 621-64-7 | N-nitrosodipropylamine | ↓ | Endosulfan I | |
| 534-52-1 | 4,6-Dinitro-2-methylphenol | | 117--81-7 | bis(2-ethylhexyl)phthalate | 210.0 | Dieldrin | |
| 87-86-5 | Pentachlorophenol | | 85-68-7 | Benzyl butyl phthalate | 40u | 4,4'-DDE | |
| 108-95-2 | Phenol | | 84-74-2 | di-n-butyl phthalate | | Endrin | |
| 65-85-0 | Benzoic acid | | 117-84-0 | di-n-octyl phthalate | | Endosulfan II | |
| 95-48-7 | 2-Methylphenol | | 84-66-2 | Diethyl phthalate | | 4,4'-DDD | |
| 108-39-4 | 4-Methylphenol | | 131-11-3 | Dimethyl phthalate | | Endrin Aldehyde | |
| 95-95-4 | 2,4,5-Trichlorophenol | | 56-55-3 | Benzo(a)anthracene | | Endosulfan Sulfate | |
| 83-32-9 | Acenaphthene | | 50-32-2 | Benzo(a)pyrene | | 4,4'-DDT | |
| 92-87-5 | Benzidine | | 205-99-2 | Benzo(b)fluoranthene | | Methoxychlor | |
| 120-82-1 | 1,2,4-Trichlorobenzene | | 207-08-9 | Benzo(k)fluoranthene | | Endrin ketone | |
| 118-74-1 | Hexachlorobenzene | | 218-01-9 | Chrysene | | Chlordane GAMMA | ↓ |
| 67-72-1 | Hexachloroethane | | 208-96-8 | Acenaphthene | | Toxaphene | N/A |
| 111-44-4 | bis(2-Chloroethyl)ether | | 120-12-7 | Anthracene | | Aroclor-1016 | N/A |
| 91-58-7 | 2-Chloronaphthalene | | 191-24-2 | Benzo(ghi)perylene | | Aroclor-1221 | N/A |
| 95-50-1 | 1,2-Dichlorobenzene | | 86-73-7 | Fluorene | | Aroclor-1232 | N/A |
| 541-73-1 | 1,3-Dichlorobenzene | | 85-01-8 | Phenanthrene | | Aroclor-1242 | N/A |
| 106-46-7 | 1,4-Dichlorobenzene | | 53-70-3 | Dibenzo(a,h)anthracene | | Aroclor-1248 | N/A |
| 91-94-1 | 3,3'-Dichlodrobenzidine | | 193-39-5 | Indeno(1,2,3-cd)pyrene | | Aroclor-1254 | N/A |
| 121-14-2 | 2,4-Dinitrotoluene | | 129-00-0 | Pyrene | | Aroclor-1260 | N/A |
| 606-20-2 | 2,6-Dinitrotoluene | | 62-53-3 | Aniline | | | |
| 122-66-7 | 1,2-Diphenylhydrazine | | 100-51-6 | Benzyl alcohol | | | |
| 206-44-0 | Fluoranthene | | 106-47-8 | 4-Chloroaniline | | | |
| 7005-72-3 | 4-Chlorophenyl phenyl ether | | 132-64-9 | Dibenzofuran | | | |
| 101-55-3 | 4-bromophenyl phenyl ether | | 91-57-6 | 2-Methylnaphthalene | | | |
| 39638-32-9 | bis(2-chloroisopropyl)ether | | 88-74-4 | 2-Nitroaniline | | | |
| 111-91-1 | bis(2-chloroethoxy)methane | | 99-09-2 | 3-Nitroaniline | | | |
| | | ↓ | 100-01-6 | 4-Nitroaniline | ↓ | | |

U indicates compound was analyzed for but not detected. This is the minimum detection limit

Table 5 Continued

Laboratory Name EPA REGION VIII

Case No

**Sample Number**

## Organics Analysis Data Sheet
(Page 4)

CLARK FORK #21
(Below St. Regis)

### Tentatively Identified Compounds

| CAS Number | Compound Name | Fraction | RT or Scan Number | Estimated Concentration (ug/l or ug/kg) |
|---|---|---|---|---|
| 1. 0001740198 | 1-PHENANTHRENECARBOXYLIC ACID, | . | 1206 | 376.0 |
| 2. | 1,2,3,4,4a,9,10,10a-OCTAHYDRO-1,4a- | | | |
| 3. | DIMETHYL-7-(1-METHYLETHYL)-, | | | |
| 4. | [1R-(1.ALPHA.,4a.BETA.,10a.ALPHA.)] | | | |
| 5. | 0.9821 MATCHING FACTOR | | | |
| 6. | | | | |
| 7. | UNKNOWN SUBSTITUTED BENZENE | | 1165 | |
| 8. | | | | |
| 9. 0000099876 | BENZENE, 1-METHYL-4-(1-METHYL | | 284 | 116.0 |
| 10. | ETHYL). 0.9811 MATCHING FACTOR | | | |
| 11. | | | | |
| 12. 0000099832 | 1,3-CYCLOHEXADIENE, 2-METHYL- | | 264 | 29.6 |
| 13. | 5-(1-METHYLETHYL). 0.9807 MATCHING FACTOR | | | |
| 14. | | | | |
| 15. | CYCLOHEXENE, 3-METHYLENE-6- | | 288 | 54.4 |
| 16. | (1-METHYLETHYL). 0.9809 MATCHING FACTOR | | | |
| 17. | | | | |
| 18. 0000544252 | 1,3,5-CYCLOHEPTATRIENE 0.8700 | . | 29 | 15.2 |
| 19. | MATCHING FACTOR | | | |
| 20. | 2-CYCLOPENTEN-1-ONE, 2,3,4- | | 322 | 24.0 |
| 21. | TRIMETHYL | | | |
| 22. | 0.9806 MATCHING FACTOR | | | |
| 23. | | | | |
| 24. 0002039909 | BENZENE, 2-ETHENYL-1,3-DIMETHYL | | 346 | 35.2 |
| 25. | 0.9810 MATCHING FACTOR | | | |
| 26. | | | | |
| 27. | PHENOL, 4-(1,1,3,3-TETRAMETHYL | | 749 | 211.2 |
| 28. | BUTYL). 0.9773 MATCHING FACTOR | | | |
| 29. | | | | |
| 30. | | | | |

There is a distinct cluster of peaks between scans 920-1280.

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